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ANALYSIS OF NON LOAD BEARING TWO COMPONENT (2K) ADHESIVES; UNDER THE AUTOMOTIVE HEMMING PROCESS VARIATIONS; THERMOGRAVIMETRIC, CALORIMETRIC AND COMPOSITION ANALYSES

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ABSTRACT

The work focuses on the analysis of non-load bearing, two component adhesives used in joining the automotive closures. The study is concerned with the thermo-gravimetric and the calorimetric attributes of the 2K adhesive. The study includes the impact of the robotic applicators capability, in terms of the mixing ratio between the resin and the hardener, and the mechanical mixing quality. A Fourier Transform Infrared Spectroscopy (FTIR) procedure analyzes the adhesive chemical groups and tracks the growth and decay of the hydroxyl and epoxy peaks. Additionally, the cure-rate based on a reaction-type, is investigated through a Differential Scanning Calorimetry (DSC). The variations in the Glass-Transition and Melting temperatures are also quantified. The Thermo-Gravimetric Analysis (TGA) quantifies the impact of holding time duration and conditions on the adhesive volatile content. Further, the final curing profile is investigated through the volatile evaporation rates. Adhesive application and bead placement is also evaluated using micrographs to ensure corrosion resistant and void free joints. Results from FTIR and DSC analyses revealed that; FTIR peaks can be used to determine mixing quality and curing behavior of two component adhesives qualitatively whereas DSC can be used to quantify it.

Keywords: Fourier Transform Infrared spectroscopy, Differential Scanning Calorimetry, Thermo Gravimetric analysis, Process audit control, Gel Point, Curing profiles optimization, Micrographs.

DEDICATION

Dedicated to my parents Sri N. Jagannadha Rao & Smt. N. V. Lakshmi, my sister Smt. N.V.D. Sowjanya

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CHAPTER 1

1.1 Introduction

Adhesives and sealants are finding wide variety of applications in today's automotive industry. Non structural and structural adhesives are used in the various parts of the automotive closures, exterior trims, interior trims and in various assemblies. Earlier days adhesives were just used as a sealer to join various assemblies, later these were used to prevent corrosion and also used in structural applications. The main reasons that motivated the automotive industry towards a wider usage adhesives and sealants are [1]:

1. Existing joining methods such as welding, brazing and fastening have many disadvantages such as, spot welding cannot be used to join aluminum, mechanical fastening cannot damp vibration and may lead to disassembly after few years of application
2. Demand to join various dissimilar materials
3. Joining light weight structures and components without compromising the structural rigidity of an automotive
4. Use of materials like aluminum, plastics and composites.
5. Multifunctional ability (Ability to join and damp vibration at the same time)

Wide variety of adhesive formulations such as pressure sensitive, cross linking and physical setting adhesives are being used in anti-flutter, hem flange bonding, glazing, interior and exterior trims etc. To give a numeric example of how these are used in today's automotive industry: The 2005 Audi A6 had an increase of 86 meters of adhesive

bonding and a decrease of 1045 spot welds [3]. Adams [4] reported that some model luxury vehicles have up to 100 meters of adhesive bonding in 2006 compared to 20 meters in 1999.

The primary focus of current research is to study the functionality of two component (2K) non-load bearing automotive adhesives. Such functionalities are mainly controlled and affected by the adhesives' rheological properties, composition, glass transition temperature (T_g), degree of cure while in storage, its sensitivity to humidity, and lastly its volatile evaporation rates. To determine the above mentioned attributes Fourier Transform Infrared Spectroscopy (FTIR), Thermo gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) procedures were used on the collected resin, hardener and 2K mix from the production lines. To reflect the changes in the mixing ratio during several shifts and between production lines; the mixing ratio of resin and hardener are varied within ± 6% from nominal (recommended by vendor) and are prepared in the laboratory for further testing.

1.2 Introduction of the different types of automotive joining methods

- Fusion- based Welding (MIG, Spot, Laser beam and resistance seam)
- Adhesive bonding
- Mechanical fastening

Fusion-Welding:

Fusion welding relies on localized heating of the substrate material to form the joint. In spot welding the current is caused to flow through electrodes and the separate pieces of the metal to be joined. The resistance of the base metal to electric current flow causes localized heating in the joint and the weld is made [7]. Earlier nearly 5300 spot welds are used to join various parts in automotive body.

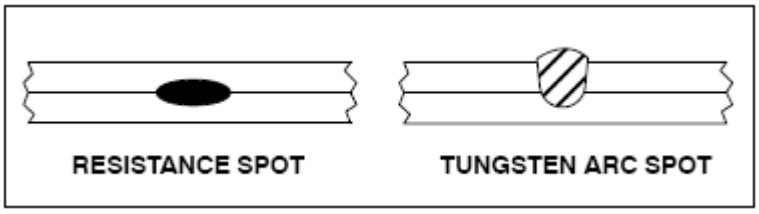

Figure 2-1: Resistance spot and tungsten arc spot welding [7]

Adhesive bonding

The adhesive bonding is gaining wide acceptance in the automotive industries around the world, replacing some fusion methods such as mechanical fastening and welding. Non-load bearing adhesives are used in hem flange bonding and as anti-flutters. Hemming is the bending of the sheet metal edge itself or over other sheet to get the nominal angle of 180^{o} [6]. This joint finds its application in automotive closure panels such as hoods, fenders, liftgates and doors. As shown in below figure 1-2 the blue region indicates the polymer based adhesive, which is generally used to join the inner and outer panel. The area shown in red is called the after-hem sealant, which is applied after the 2K adhesive has been fully cured, to prevent any moisture or chemical ingress.

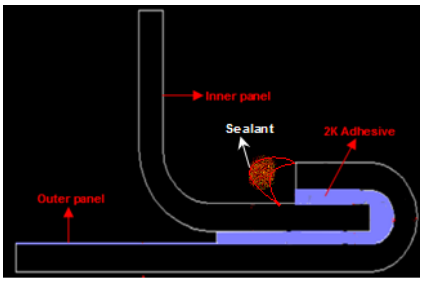

Figure 2-2: Hem joint

Mechanical joining:

Self piercing rivets and clinch joints are two types of fasteners [9] that are used to join automotive bodies. Self piercing rivets do not pierce into two panels to be joined instead it pierce into upper panel of the joint and rivet expands in the inner panel to create mechanical interlock as in figure 1-3. Unlike self piercing rivets, clinch joints never use rivets, instead both upper and lower panels are formed between the punch and a die as shown in the figure 1.4 [9].

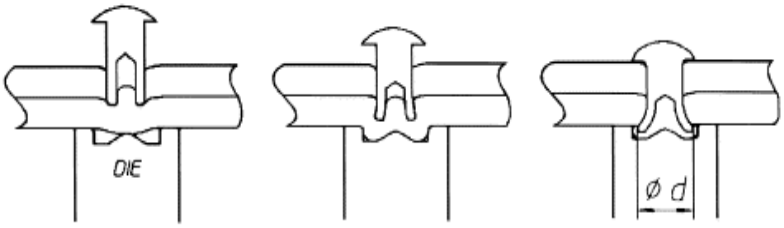

Figure 2-3: Self piercing rivets

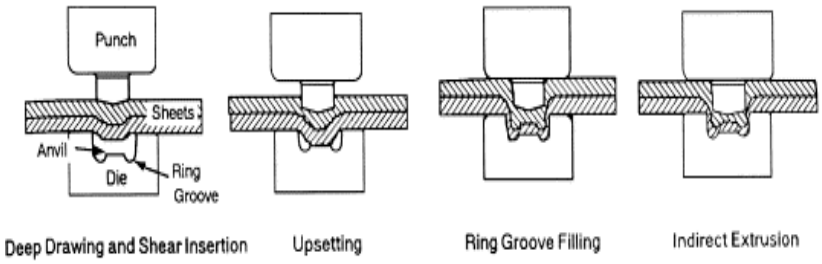

Figure 2-4: Clinch Joints

1.3 Adhesive bonding compared to other joining methods

	Welding	**Fastening**	**Soldering**	**Adhesive bonding**
Corrosion	May corrode in long term	Corrodes in the regions nearer to bolt	Can be eliminated if corrosion causing flakes are removed	No or less chance of corrosion
Stress distribution	stress due to local stress points	Stress are concentrated around single point	Fairly good stress distribution	Excellent stress distribution
Vibration damping	Cannot damp vibration	vibration loosens this joint	Good vibration damping ability	Acts as excellent vibration dampers
Cost	High cost equipment and energy costs	Fairly cheap equipment	Manual equipment is cheaper than the automatic	Cost depends on application.
Resistance to higher temperatures	Offers good resistance	Offers good resistance	Depends on filler material	Poor resistance
Permanence	Permanent	Not permanent	permanent	Permanent
Materials joined	Only same kind of materials joined	Different kind of materials can be joined	Little bit capable	Highly capable of joining dissimilar materials
Joint appearance	Some kind of dressing is necessary	Leads to uneven surface	Fairly good	Joint generally unseen
Surface pretreatment	Little surface pretreatment is necessary	No surface pretreatments are necessary	No or little surface pretreatment	Surface pretreatments are necessary

Table 2-A: Comparison between various joining methods

1.4 Polymeric adhesives and sealants

According to Petrie [1]: *"An adhesive is defined as a substance capable of holding at least two surfaces together in a strong and permanent manner",* while a sealant; *"An sealant is a substance capable of attaching at least two surfaces, therby filling the space between them to provide a barrier or protective coating"*

In earlier days vegetable oils and fats, seed oils, starch, animal bone glues were used to join two surfaces. With the advancements in the polymer science and technology many properties of the polymers supporting adhesion came into light.

Polymer adhesives offers following advantages

1. Low cost and weight
2. Good appearance.
3. Excellect moisture and chemical resistance
4. High strength and toughness values
5. Good insulation properties

In addition to all the above advantages, polymeric adhesives offer viscoelastic behaviour by virtue of which movement upon application of load is posssible. Desired properties for example increased tack or ductility can be introduced into the polymeric structure by adding additives such as tackifiers or plasticizers. Addition of additives depends on the end properties required . A major disadvantage with the polymers is that their physical properties are highly dependant on temperature. Strength of these materials decreases with increase in temperature and lack stiffness when compared to metals [2] . Typical applications of polymeric adhesive include transportation, medicine, paper amd

packaging sector. In automotive industry wide variety of adhesive formulations such as pressure sensitive, cross linking, physical setting are used in lining of interior linings, bonding at cabriolet soft tops,bonding of brake pads and shoes, hem flange bonding,anti flutter bonding, direct glazing, outer trim parts, side projecters, name plates, direct glazing, boot linings, sound, heat insulation parts etc [5].

1.5 General classification of adhesives and sealants

Adhesives can be classified based on their formulation source into; naturally occurring adhesives and synthetic adhesives. The naturally occurring adhesives such as Dextrin, cellulose, starch, animal glue, natural rubber and Casein are few examples of non synthetic adhesives. While the Classification of ***synthetic or manmade adhesives*** might be based on the load bearing capability as:

- ***Structural adhesives:*** Generally used in the *a*pplication that requires resisting huge loads
- ***Non-structural adhesives:*** These adhesives are generally used to hold two substrates together. They fail when used for high load bearing applications or at adverse climatic conditions such as extreme temperature and humidity. For example, Epoxy based adhesives are generally classified as structural, Anti flutter (rubber based adhesives) as semi-structural, screen bonding adhesives can be classified as low or Non structural adhesives [4].

Other classifications include: The Chemical composition:

- ***Thermoplastic adhesives:*** Thermoplastic adhesives can be softened by the application of heat (i.e. above their glass transition temperature (T_g). These kind of adhesives generally have branched or linear molecules as backbone which can be easily broken by the application of the heat.
- ***Thermosetting adhesives:*** Unlike thermoplastic adhesives these adhesives become hard and brittle upon application of heat (i.e. above their glass transition temperatures). Cross linked structure is formed by application of heat. Overheating may lead to degradation due to the oxidation.
- ***Elastomeric adhesives:*** Elastomeric adhesives return to their original positions once the deformation load is removed. These kinds of adhesives are generally used for sealants (PVC), vibration dampers and sound insulators.
- ***Hybrid adhesives:*** As stated in section 1.2, here adhesive or sealant is generally blended with the several additives or fillers to make it suitable for the required application. For example fillers such as aluminum powder, carbon black, zinc and silica are generally added to reduce the shrinkage of adhesive at high temperatures [1]. Likewise, today's research is much focused on developing the hybrid adhesives to improve the adhesive properties such as toughness, ductility, resilience, fatigue, peel strength and electrical conductivity.

  The Physical form classification of adhesives or sealants includes:

- ***Liquid adhesives with solvent:*** Solvents such as water and ethanol are added to the adhesive to control rheological properties thus making it spreadable on the flat surface
- ***One component solvent-less adhesive*****:** One component (1K) cures by either *a*pplication of heat or by the influence of external agents.
- ***Two component solvent-less adhesive:*** Unlike 1K, two component *(2K)* comes with the base component resin and hardener or catalyst which influences the former to cure at room temperature. Post cure methods such as induction curing (discussed in chapter 3.5**)** may be employed to obtain the comp**l**ete cure.
- ***Solid adhesive****:* Powder, crystal, form and tape adhesives fall under this category.

Sealants:

In terms of sealants; it is typically classified based on their hardening mechanisms and physical forms. This Report discusses about two component (2K); Thermosetting, non load bearing epoxy adhesive and heat cured one component (1K) elastomeric sealant.

1.6 Classification of adhesives in the automotive industry

Primary classification of automotive adhesives is according to type of cure employed, place of application and the final strength requirements. Automotive adhesives fall into following categories [5]:

(a) Rapid set at room temperature, which include Anaerobic and Cyanoacrylate adhesives Applications include gaskets, bonding of electrical and electronic items, thread sealing, bonding of caps in cylinder head covers and gear boxes. (b) Rapid set at high

temperature: Epoxides and phenolic adhesives fall into this category. The applications include bonding of heat exchanger and hem flange adhesive. (c) Evaporation of moisture, which comprise Synthetic resin sealants with applications include gaskets, Anti- flutter and common sealing. Further types include; (d) Set under application of external pressure such as Pressure sensitive tapes used in bonding of name plates, mirrors, reflectors etc. Lastly, (e) Encapsulated adhesives, which cures anaerobically or with the bursting of capsules and are used in fastener locking applications. Classifying the adhesives from the intended application perspective can also include;

Anti Flutter adhesives: Anti flutter adhesives are generally applied to fill the wide gaps between the inner and outer panels [4]. Secondary functions of anti flutter adhesive are to damp vibration and noise and increase the stiffness of attached parts. Generally rubber based butyls and epoxy modified polymers are used as anti flutter adhesives.

Adhesives for bonding of trim assemblies (Non structural adhesives); Non functional metal or plastic moldings or other accessories, which are mounted to fully painted car are generally called as trim assemblies e.g. bonding of screens, emblems etc. Generally pressure sensitive tapes or cyanoacrylates are used for this purpose [4]. Polyurethanes, silane polymers with a polyurethane backbone are generally used in the wind screen bonding because of their good adhesion to the painted surfaces.

Power train adhesives; Anaerobic acrylates are generally used in shaft to hub connections and silicones are used frequently to form gaskets.

Crash resistant adhesives; Research in this area showed that rubber particles dispersed in the epoxy matrix showed good crash resistant behavior than the commercial epoxy [4]. Thermosetting polyurethanes and acrylics can be used to obtain required crash resistance.

1.7 Factors that influence the selection of automotive adhesive or sealant

1. Type of application.
2. Joint type
3. Nature and type of substrate
4. Curing methods employed
5. Cost
6. Type of stresses that it should sustain
7. Time frame between the application or curing process (Holding time)
8. Handling strength (Time to attain green state)
9. Application type (Brush, trowel, Robot applicator etc,.)
10. Desired physical properties (Tough, Flexible etc.)
11. Surface pretreatment or preparation.
12. Used as such or used with other joining methods such as bolting, riveting etc.,
13. Storage time before application (Shelf life)
14. Washout stability if no immediate curing is applied.
15. Sag resistance values
16. Pot life or reaction time in case of 2K adhesives

17. Shelf life of adhesives. (Viscosity generally doubles once adhesive exceeds pot life).

1.8 Formulation of adhesives or sealant

Present day adhesives and sealants need to perform special functions. So the adhesive formulation and additives are decided according to the final application main attributes, such as operating temperature, humidity, and force. The adhesives additives influence its behavior through improving or modifying some of its attributes; such as: reducing the thermal expansion, controlling its rheological properties, improving or reducing the thermal and electrical conductivity based on the application, Improving its tack and toughness, and lastly increasing its working temperature range. Additives are typically classified into:

Primers: Primers form the thick layer of coating on the substrate surface to promote the adhesion between the adhesive and its substrates. Through one of following functionalities:

- Increases surface energy of the substrate
- Acts as corrosion inhibitor
- Helps in increasing the joint strength
- Primers provide required wettability for the adhesive.
- Keeps surface fresh if longer hours of storage before assembly is required.

Optimum thickness should be maintained to harness the desired properties of the primer.

Adhesion Promoters: Adhesion promoters may or may not be integral part of the adhesive. It acts as a primer in some application. The only difference between the primer and adhesion promoters is that the former forms a thick layer and the latter forms the monolayer. It forms a strong covalent bond between the adhesive and the substrate thereby preventing the water, oxygen or the salts ingress into the joints, when used under adverse conditions. These are also called as coupling agents. Typical examples include phosphorous containing compounds [10].

Accelerators: Accelerators increase or decrease the rate of reaction, curing rate, storage and working time as per the application.

Solvents: Solvents such as ethanol, water, and acetone are generally used to decrease the viscosity of the base resin thereby increasing its spreadability on the substrate surfaces.

Thixotrophic agents: Thixotrophic agents are generally introduced to enhance the sag resistance of the adhesive so that the adhesive bead remains in position, when applied on vertical substrates.

Diluents: Unlike solvents, diluents do not evaporate after application. Reactive diluents react with the binder in the initial stages.

Tackifiers: Tackifiers are generally used to increase the green strength of the adhesive thus improving the handling strength which is necessary in assembly shop before post cure.

Fillers: Fillers improve the desired properties of an adhesive such as strength, working properties, electrical conductivity and corrosion resistance

***Plasticizers*:** The ductility of adhesive increases with the addition of plasticizers. These are part of the ingredients that are added to the base resin.

Tougheners: Tougheners impart the required impact resistance and mitigate crack propagation. 2K epoxy adhesive generally fails in peel (Discussed in detail in section 1.9). So, it is imperative to introduce tougheners into the base resin matrix of the adhesive to improve its peel resistance, e.g. Nitrile rubbers. Other ingredients such as antioxidants are used to delay the aging of the adhesive.

Sealants:

Solvents help to increase flowability or gunnability (Sealant guns are generally used to apply sealant) of the sealant by reducing the viscosity. Hydrocarbons such as Xylene, toluene, ketone are used for this purpose. Other additives such as thixotropic agents, fillers, antioxidants. Plasticizers are used to modify the sealant physical and chemical properties.

1.9 Types of stresses in adhesive joints

Thermal stresses: These stresses are generally created due to heat curing of adhesive. When adhesive is cured and cooled, adhesive which has more coefficient of thermal expansion (CTE) than metal substrates contracts more than the metals. Also, composite Joints (materials with the different CTE's) induce more stress than that of the material with the same CTE's.

Hygroscopic or swelling stresses: These stresses are generally introduced due to the entrapment of moisture in the joint during mixing, holding or transportation.

Mechanical stresses in the joint:

Peel stress: Peel stresses in the adhesive joint arise due to the action of perpendicular forces. Adhesive joint fail more in peel than that of shear

Shear stress: Shear stress in the adhesive joints is due to the action of parallel forces as shown in the figure 1.5. Voids, bubbles and contaminants in the adhesive may also leads to stresses in joints.

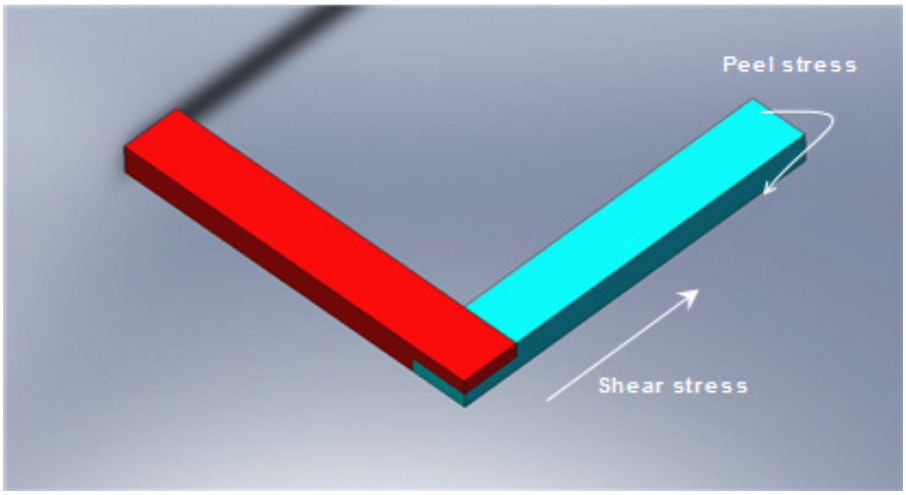

Figure 2-5: Mechanical stresses in adhesive joint

CHAPTER 2

2 Literature Survey

The present literature survey is focused on three main sections: the automotive adhesives curing and its associated defectives, the hemming process, and the thermal analysis techniques and studies.

2.1 Basics adhesives and sealants

Baldan et al in [2] discussed the different types of polymeric adhesives and sealants to include polyurethanes, epoxies, silicones, acrylates, hot melts and anaerobic adhesives. He also discussed the various application and specific properties of each kind. Petrie et al [1], Adams [4] and Pizzi & Mittal [5] provided comprehensive surveys about the different types of polymeric adhesives.

2.2 Curing

Wu et al [19] has provided a study covering the curing characteristics of automotive two-component adhesives, when cured using induction coils. In [19] the variations in the bonding strength with relation to variations in the industrial ovens are also discussed. The study indicate that the ramp up rate control is important, maintaining a steep rate (greater than 50^{o}C) during initial stages is required to achieve rapid hardening of adhesive. This might resolve some issues such bubbles oozing (popping) out. However, these rates might also lead to incomplete cure. In the study, a low carbon steel with 2K epoxy based adhesive is subjected to different ramp up rates of 10, 50 and

100°C/min for five seconds, which is enabled through an induction based curing. Results showed that increasing the heating rate to 1000°C/min for a short span of time increased the bonding strength. Increasing the holding time (inside the fixture) will increase the bonding strength initially, but found to decrease at later stages. Regarding the curing peak temperature, the prescribed bonding strength is attained at 80°C which is much lesser than the vendor prescribed peak temperature. In regard to adhesive bubbling while curing, the publicized literature provides three important reasons behind the bubble formation in the adhesive bead.

1. Phase transformation of compounds from solid to gaseous
2. Thermal expansion of gas voids
3. Chemical reaction which leads to gas phase

Also, the literature provides some countermeasures to control the bubble formation; through increasing the ramp up rates during the initial stages of curing, and by increasing the holding time (while in fixture) to get the required bonding strength.

However, in regard to voids formation inside convection based curing; the rate of cure (DSC and FTIR), the amount of contraction and expansion, and the denseness of the 2K adhesive used (Viscosity tests) can be used to quantitatively describe this phenomenon. The effect of curing on viscosity and mechanical properties is discussed by Laprique et al in [18]. The objective of that study is to analyze the variations in the rheological and the mechanical properties of the adhesive, when manipulating the curing peak temperature. The study uses two-component adhesives (room temperature cured), which is then subjected to different peak temperatures 23°C, 45°C and 64°C. Aging test is also

performed to study the properties of adhesive in the extreme weather conditions. The findings from [18] can be summarized into:

1. If the 2K adhesive is cured below its glass transition temperature then its network will vitrify thereby stopping further curing or reaction in an adhesive. (Vitrification is the stage where mobility of the molecules ceases there by stopping the further reaction)
2. Higher ramp up rates in the oven generally raises the glass transition temperatures of adhesive.
3. Post curing at higher temperatures by external means such as induction heating or oven curing increases the curing rate of adhesive.
4. Near gel point of the adhesive, its viscosity increases abruptly, which also increases the molecular weight of the adhesive
5. Too much exposure to humidity conditions may soften the adhesive leading to less rigid joint.

Chang et al [20] discussed advantages of post curing the adhesives. Main observations are; post curing the 2K room temperature adhesive improved its recoverability, while increasing its modulus, and upper yield limit and lower yield limit. This is due to the increase in the relaxation ability. However, excessive post curing may also lead to degradation and evaporation of volatile substances from the adhesive. Petrie[1] in his report discussed the advantages of the electromagnetic curing when compared to conventional methods.

2.3 Hemming

The basics of the hemming process and its different variations, and possible defects are discussed in details in [21-23].

2.4 Thermal analysis techniques

References [1, 4 and 5] provide the fundamentals of the thermal analysis when used for investigating the adhesives rheological properties. Additionally articles from [25] provide further information in regard to available systems' capabilities, samples preparation and the general guidelines. Following provide the specific referenced work for each one of the techniques utilized.

FTIR: Bhatia et al [17] investigated the epoxy characteristics of a resin blend, using its specular, reflectance and the spectrometric, with focus on the 911 cm^{-1} peak. Furthermore, Bhatia et al studied the variations in 1296 cm^{-1}peak with the epoxy reaction. Sharma et al [15] analyzed the reaction kinetics and the non-thermal effects due to ultrasonic curing methods of epoxy resin. In his report, main observations are based on the variations in the 911 cm^{-1} epoxy group. He observed that as the reaction between resin and hardener opened the epoxy ring; it raises the hydroxyl peaks 3350-3500 cm^{-1}. Also the reaction mechanisms are further explained in reference [14]. According to Bockenheimer et al [16] the peak growth in the region of 1770 to 1620 cm^{-1} can be a good indicator of the epoxy group concentration. All the above mentioned peaks are analyzed in this study.

Other literature covering the topic of structural adhesives is in [26, 27 and 28]

CHAPTER 3

3 Process flow

3.1 Introduction

This section illustrates the adhesive application process flow, starting from the hemming side and continuing into the final assembled component. The introduction explains the material used and the process flow. Additionally, some technical terms are defined. Further sections in this chapter introduce some issues related to adhesion and surface preparation.

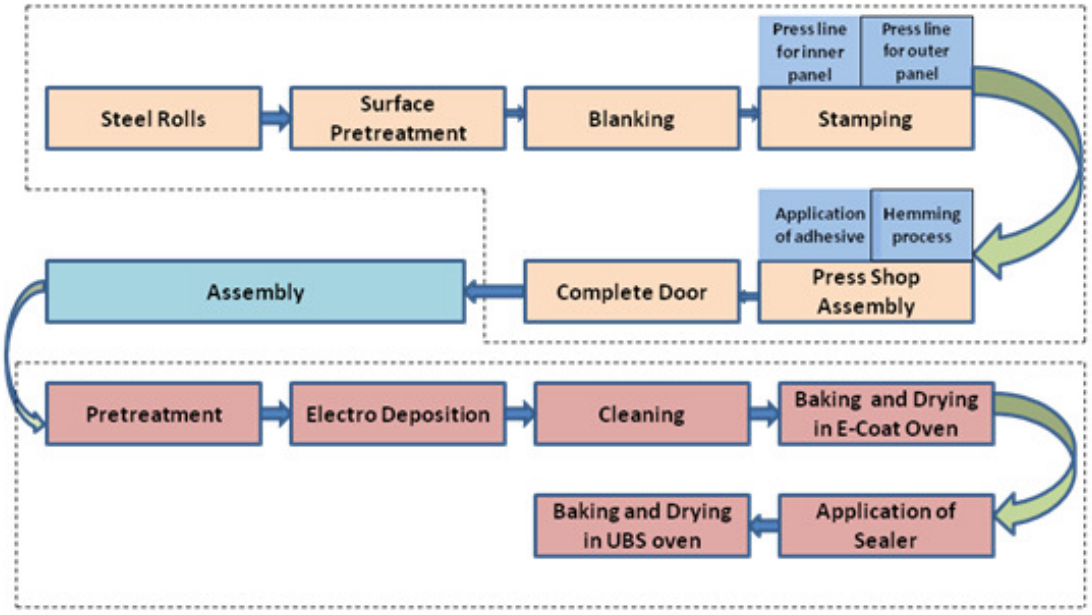

Figure 3-1 Material flow in automotive door manufacturing process

Steel rolls: Different types of steels such as hot-rolled, uncoated, cold-rolled, hot dip coating, deposition of zinc or other organic compounds, electroplating are used in

automotive press shops for the production of inners and outers of automotive doors, hoods and lift gates.

***Surface pretreatments*:** Automotive lubes or Hydrocarbons mixed with water are generally used to wash blanks, to remove dirt or contaminants that are deposited during transport from steel mill or storage.

Blanking: Blanking is the process by which steel roll is straightened to remove residual stress induced during rolling process in steel mill. Here blanks are dimensioned and sliced according to final requirements. The blanking is followed by stamping, which is a forming process that uses multiple press stations to perform trimming, piercing, bending, etc., on sheet metal. Number of press stations depends upon the number of operations needed to get the desired shape. Generally inner and outer panels are stamped on the different press stations and stacked near assembly cell for assembly.

Application of adhesive: Two component (2K) adhesive will be metered and mixed using static mixer. It is then applied using adhesive application robots as a circular bead on the door outer flange. More details about the adhesive application step are in section 3.4.

Hemming station: Inner and outer panel with the adhesive bead are assembled in the hemming station. This is done by bending the edge of sheet metal over itself or over other sheet to get the nominal angle of 180^{o}. This process is exclusive for joining inner and outer panels of automotive closure panels such as doors, hood, lift gates, fenders etc,. The primary function of this process is to: Join inner and outer panels and Provide uniform and good appearance for final joints. The Hemming process sequence generally

involves three stages flanging, Pre hemming and hemming; Flanging bends the panels to 90^{o}, followed by the pre-hemming stage, which further reduces the angle of the outer panel flange. Lastly, the hemming bends the panels into 180^{o} angle (figure 3-2).

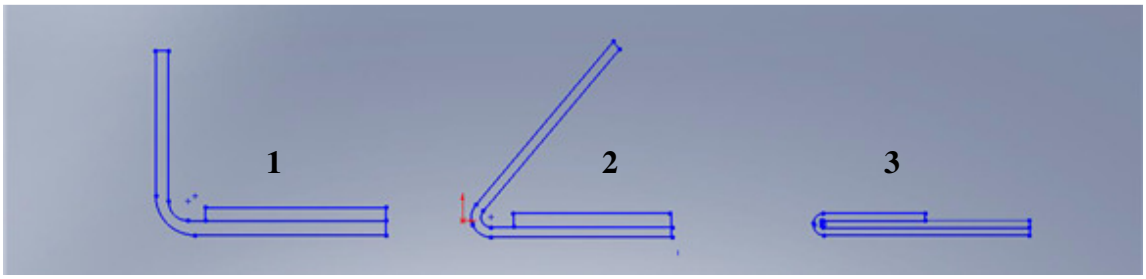

Figure 3-2: Three stages of hemming process 1) flanging 2) Pre hemming 3) Hemming

Curing (Press shop): Doors are sent through the pre-curing oven where short exposure (10 minutes) to temperatures of 100^{o}C – 200^{o}C provides the sufficient handling strength to the adhesive.

Assembly body shop: Completed doors from the assembly shop are assembled to form the body in white structure.

Electro-deposition coating: Before entering into paint shop the Body in White (BIW) is pretreated (through aqueous and acidic cleaning agents) to remove contamination, slug, dust, press marks etc. This is important because if the surface is not clean, any surface irregularities will be exaggerated through the paint (tele-graphing). Additionally, the paint adhesion will be affected. After pretreatment and phosphating (conversion coating) of the substrate; electrodeposition coat (E-Coat) is applied through immersion tanks. It acts as a foundation for the subsequent coats (base coats and finish coats) and also it acts as a good corrosion resistance.

E-Coat oven: E-coat oven is generally programmed to higher temperatures to cure not only the E-coat but also the pre-hem adhesives. The E-coat curing profiles comprise three steps; ramp-up, steady-state and cooling.

Sealer application: Generally elastomeric sealant is applied along edge of the hem joint to make the joint air tight, moisture tight and to prevent the external contamination entering into the joint. Finally the sealant oven is used to cure elastomeric sealant.

3.2 Theory of adhesion

Surface energy, surface tension and surface roughness of substrate are the main factors, which affect the wettability of the adhesive. Wettability is defined according to Baldan [2] as the thermodynamic work of adhesion (W_a) for the seperation of solid from liquid, decribed in equation (3.1):

$$W_a = \gamma sv + \gamma lv - \gamma sl \quad (3.1)$$

Where γsv = Specific surface energies of solid vapor interface

γlv = specific surface energies of liquid vapor interface

γsl= Specific surace energies of solid liquid interface.

Young's equation can also be used to correleate between the surface tension and contact angle . As shown in the figure 3-3 below, and mathemtically in equation (3.2), which is the result of balancing energies in all the directions

$$\gamma lv \cos\theta + \gamma sl = \gamma lv \quad (3.2)$$

where θ = contact angle

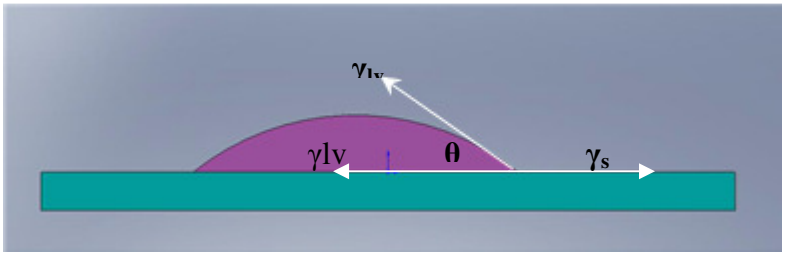

Figure 3-3: Contact angle of surface liquid

Complete or partial wetting is possible when 0 < θ < 90 i.e γsv>γlv+γsl; Here in this case the S-V is completely replaced by the L-V and S-L . No wetting is possible 90< θ<180 i.e γsv+γlv<γsl here S-L interface is replaced by S-V and L-V. Combining both equations (3.1 and 3.2) yeilds a relation between the contact angle and the thermodynamic work of adhesion, in equation (3.3)

$$W_a = \gamma lv\ (\ 1+ \cos\theta) \qquad (3.3)$$

Measuring the surface energies on-site can be done through using dyne test markers, without having to measure the contact angle using a goniometer.

3.3 Surface Pretreatment

Adhesion occurs only when the substrate condition is favorable and its surface energy is high enough to accept (spread) the material (adhesive, paint) on it, to form the bond necessary for adhesion. Different surface preparation methods are employed to enhance surface energy and modify its chemical structure. The above mentioned conditions are necessary to create atmosphere amicable to the adhesive. For a good

adhesion surface free energy of the substrate ($\gamma_{substrate}$) should be more than that of the adhesive ($\gamma_{adhesive}$) i.e., $\gamma_{substrate} >> \gamma_{adhesive}$

The surface energy value of galvanic zinc coated steels is approximated around 70.8 mJ/m^2 when compared to epoxy 46 mJ/m^2 and PVC 41.5 mJ/m^2

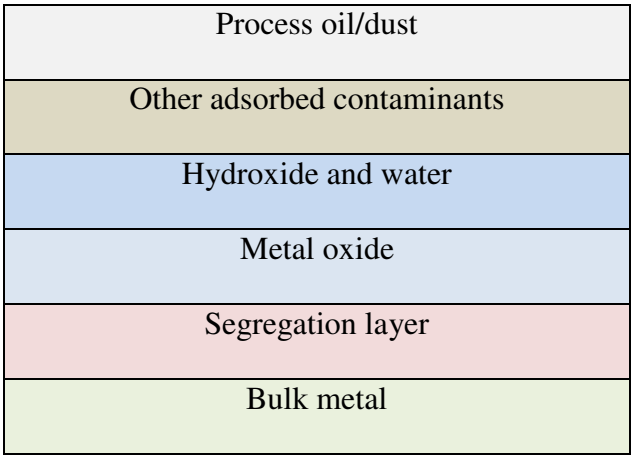

Figure 3-4: Different layers on bare metal surface

Figure 3-4 gives the details of the layers that are present on the bulk metal, some of which need to be removed to provide for good adhesion. These layers can be formed during the production processes of metal, storage, atmospheric conditions, shipping and handling of the metal substrates. Few of the surface preparation methods are [4]

1. Solvent degreasing
2. abrasion
3. Grit blasting

→ Physical methods

4. Chromic acid etching
5. Anodizing (Chromic and phosphoric acid)

→ Chemical methods

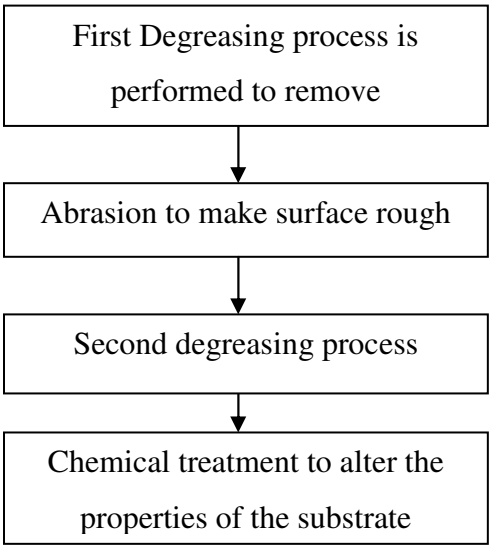

Figure 3-5 : Pretreatment process flowchart

The above flow chart (3-5) is a general representation of a typical treatment process. Some steps can be added or removed depending on the end usage of the assembled product. Following factors greatly influence the sequence; Ultimate bond strength, the type of material, surface, Service environment, and the Life cycle of the end product. Following describe each one of the pretreatment steps.

Solvent degreasing: Oils, greases and other oxides can form weak layers which obstruct the adhesion process. Hydrocarbons distillate (Major percentage) with the minor percentage of corrosion inhibitors (also called as wash) can be used as solvents to remove the grease and other dirt particles.

Abrasion: Abrasive or emery paper is used to roughen the surface thus increasing the contact area of the adhesion. Utmost care should be taken that roughness values stay within the specified values. Excessive roughness may lead to stress concentrations.

Grit blasting: In this process highly accelerated abrasive or sand particles hit the surface thereby preparing the surface for bonding and subsequent finishing.

Etching and anodizing: Etching and anodizing improve the surface chemistry, making the surface chemistry more compatible to the adhesive formulation. The thickness of metal oxide layers can also be controlled through this process.

The improvement in lap shear strength of the epoxy bonded, cold rolled steel substrates due to surface pretreatment is shown below (Table 3-A) [1]

Type of treatment	**Lap shear strength (psi)**
As received	2900
Vapor degreased	2910
Grit blast	4260
Acid etch	4470

Table 3-A: Improvement in shear strength with pretreatment

3.4 Adhesive application processes

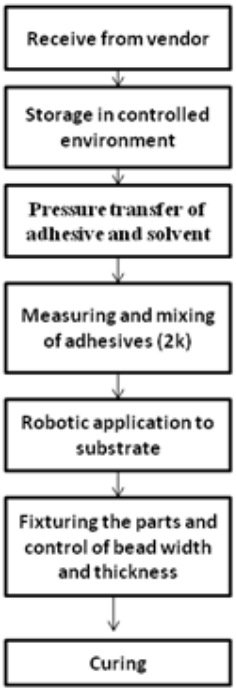

Figure 3-6 : Adhesive application process flow chart

Viscosity of adhesive should be monitored and recorded to set the robotic mixers and applicators accordingly. Additionally, to further control and maintain adhesives and sealants viscosity, it should be stored in a controlled environment. Additionally, this minimizes the volatile evaporation during storage. Care should be taken that the adhesive barrel should be used within its shelf life. After the shelf life expires, the adhesive viscosity doubles. Following text describes some of the issues associated with the handling, mixing and application of the 2K adhesives within the automotive production lines.

Pressure transfer of adhesive or sealant:

Pressure transfer of adhesives and sealants is a good method when compared to mechanical transfer because if one component adhesive is transferred using latter method the friction within the surfaces causes the flowing fluid to polymerize and cure. Transfer distances should be maintained in such a way that it does not affect the rheological properties of adhesive. Proper cleaning of hoses or flow pipes should be ensured before application.

Measuring and mixing of a two component adhesive:

Accurate measurement of the two-component adhesive resin and hardener is vital because if the catalyst or initiator percentiles are not accurate, it affect the adhesives brittleness (catalyst too high) and its cure rate. For a sound joint it is necessary to mix both initiator and resin in correct proportions. Utmost care should be taken while mixing because any air entrapment may cause adhesive to foam after the E-coat or sealant ovens. Degassing should be performed if adhesives are mixed in room temperatures and humidity conditions.

Control of bead width and thickness:

Inline CCDs are used in assembly cells to track the variations in bead placement. If any change in flow rates is found through destructive checks or a change in viscosity is observed, the application speed is varied to compensate for the deviation. Several factors should be considered before or during application of adhesive including; Lube oil or the press hydrocarbon oil should not be present (concentration more than 3-4 grams/m^2) on substrate [4]. This influences the positional stability of bead and its adhesion strength.

Although the viscosity during application of adhesive is reduced for the ease of application, the adhesive should be capable of regaining its viscosity to maintain bead position and width. Also, to give sufficient handling strength and wash out resistance, the adhesive should be pre-cured. The adhesive pumping distances should be within range to keep rheology of the sealer within prescribed limits. And lastly, if the adhesive is applied intermittently instead of continuous beads, phenomena such as stringing or tailing should be monitored.

3.5 Curing

Final Curing: Traditional heating processes employ oven curing through one or a combination of the three heat transfer modes, conduction, convection or radiation. A typical problem in convection based ovens is the non-uniformity in the temperature gradients across the substrate. Recent advancements in this field have paved the way for new inventions. One such invention is electromagnetic curing as in Microwave chamber curing. Also, induction heating, which employ variety of coils through which current is passed generating eddy currents to act as a heat waves. Uniform heat distribution is possible with this type of heating.

2K Adhesive chemistry:

Epoxy Resin*:*

Epoxy is available in single component heat cured adhesives or in multiple component reaction cured adhesives. It is versatile because several formulations are available to suit the application. Epoxy based adhesives have higher cross linking density

at higher temperatures. It has low surface energy value which allows it to adhere to different types of substrates. Good adhesion may be due to the presence of hydrogen bonds in its molecular structure and good wettability may be attributed to the presence of hydroxyl groups. Because of its thermosetting nature, it has better tensile strength in tension but fails in peel. The basic structure of the adhesive under investigation is based on Diglycidyl ether of bisphenol A (DGEBA) displayed in figure 3-7. This composition is identified through an FTIR analysis. Further, FTIR spectra of the resin sample, which is used to identify the different functional groups, is shown in figure 3-8. Analysis showed the presence of DGEBA molecules in it. The amount of DGEBA can be computed by evaluating the 911cm^{-1} peak. For the hardener analysis, the FTIR revealed that the hardener is a Tetra hydro furfuryl methacrylate (THFMA). THFMA acts as adhesion promoter. A basic structure and FTIR spectrum of the hardener sample is shown in figures 3-9 and 3-10 respectively.

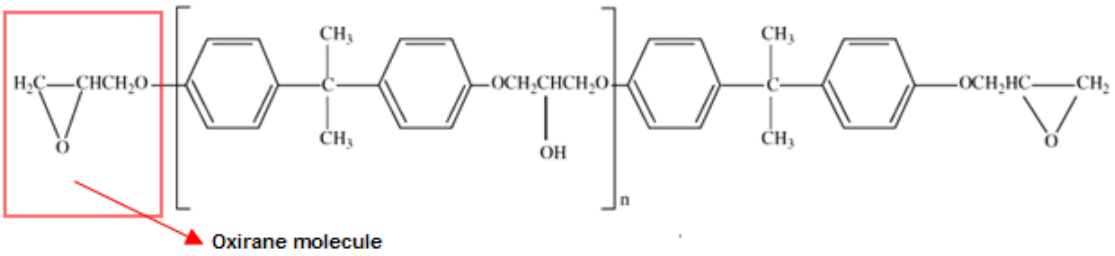

Figure 3-7: DGEBA molecular structure [1]

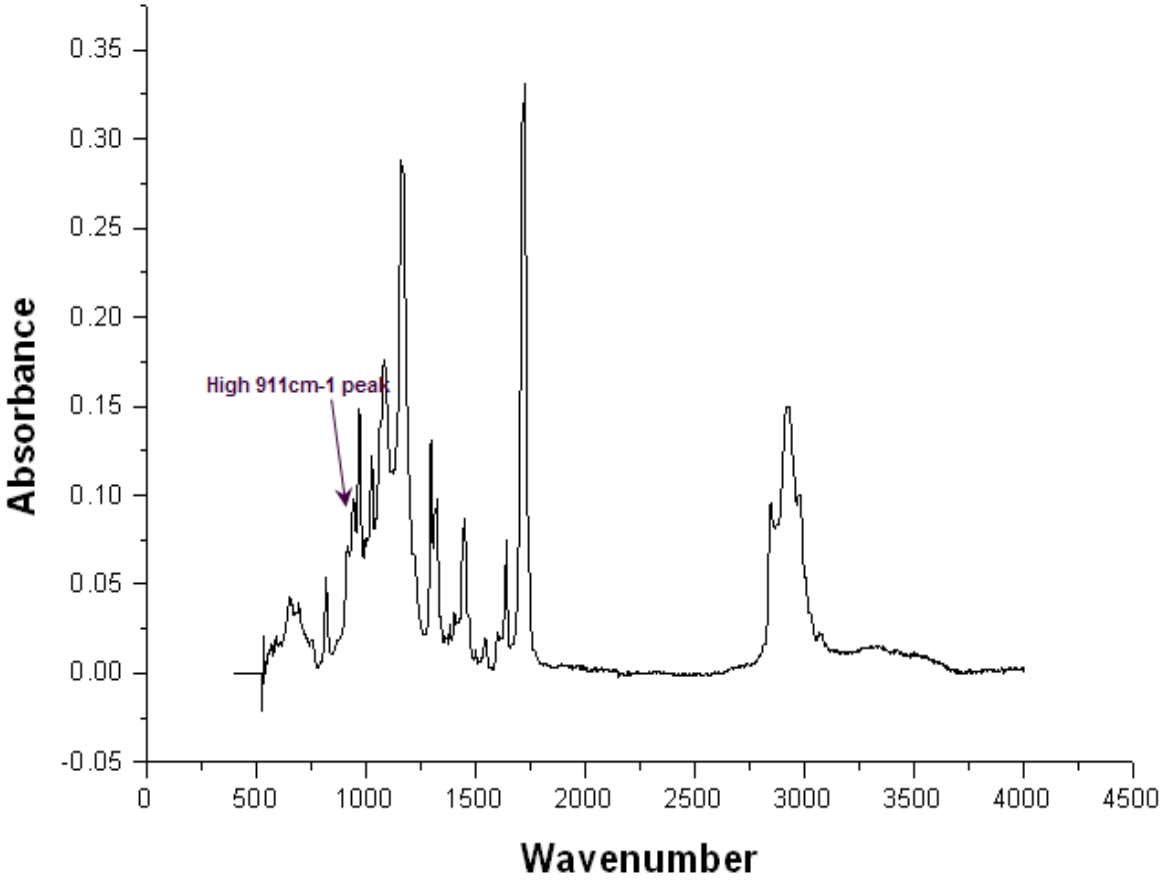

Figure 3-8: FTIR spectra of resin sample

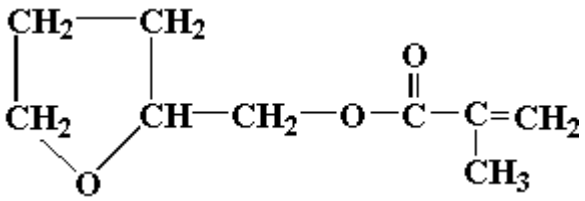

Figure 3-9: Basic Representation of hardener (Tetra Hydro Furfuryl Methacrylate (THFMA) [11]

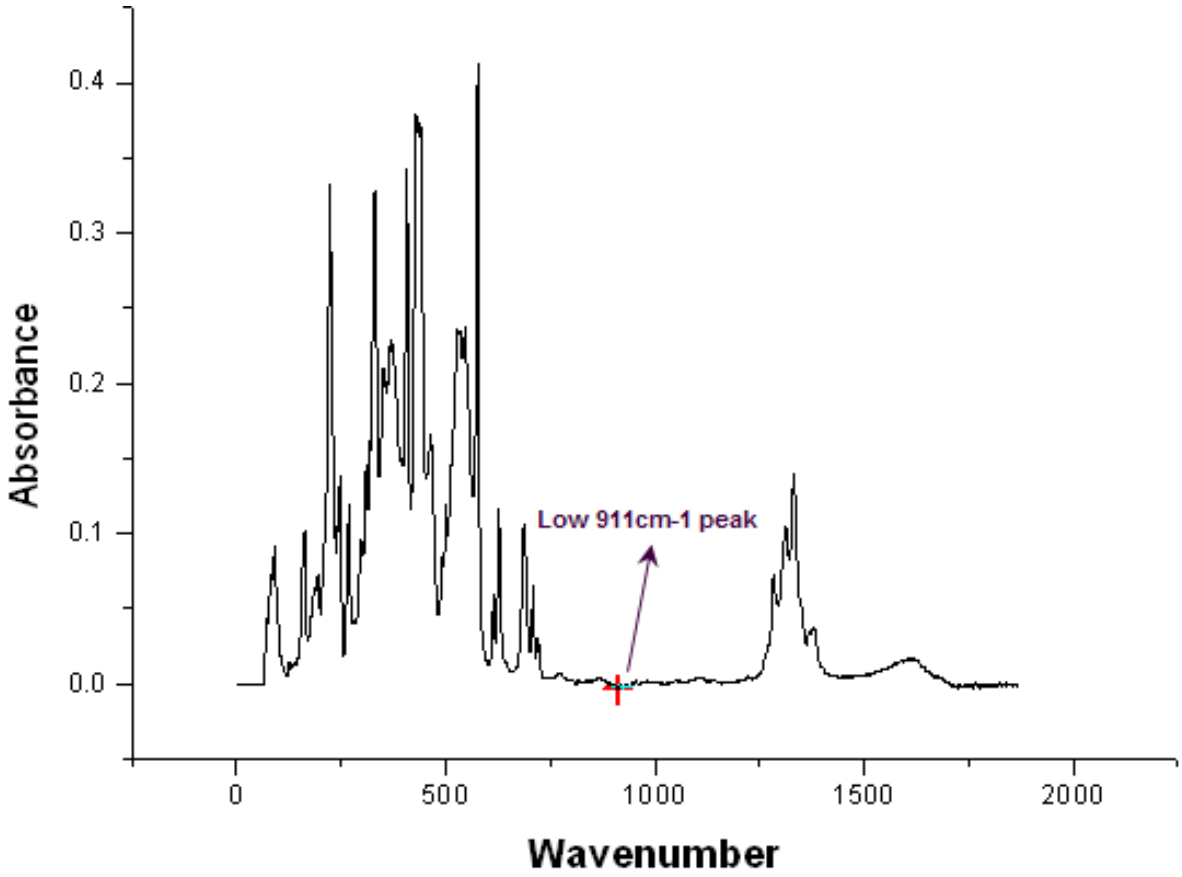

Figure 3-10: FTIR spectra of hardener sample

Reaction between DGEBA and THFMA.

When hardener (THFMA) reacts with resin (DGEBA), the oxirane ring as shown in the figure 3-7 opens, leading to the formation of hydroxyl groups and the degradation of epoxy group. As the reaction proceeds the epoxy percentage in the final product decreases and the hydroxyl percentage increases. The extent of this reaction can be evaluated using the FTIR spectra and the DSC curves.

CHAPTER 4

4 Laboratory tests

This chapter evaluated the impact of the process variations on the 2K adhesive, rheological and mechanical attributes, and its impact on the final hemmed joint. Following factors will be evaluated; Viscosity, Bead placement, Moisture entrapment, Storage conditions, Surface contamination, Holding time, Curing rate, Presence of solvents, and Mixing ratio of resin and hardener.

4.1 Sample preparation

As mentioned in section 1.1, upon studying four different production cells in an automotive press shop, a fluctuation of ±6% is found in the adhesive mixing ratios. So following samples are prepared in different mixing ratios on weight basis:

1. 3.5 (Resin): 1 (Hardener)
2. 3.5 (Resin) : 0.75 (Hardener)
3. 3.0 (Resin) :1.0 (Hardener)
4. 3.5(Resin) : 1.5 (Hardener)

All the above mentioned samples are measured using table top digital tare balance and are mixed using steel spatula and ceramic bowl. The two-component mixture should be free from air. Entrapped air may cause voids in the adhesive and make it foam, when the latter is exposed to higher temperatures. So when two component adhesives are mixed in room temperature and conditions, vacuum degassing should be performed to remove

any entrapped air. To see the variations with holding time, the above mentioned samples are closed in glass vials, which in turn stored in well conditioned laboratory environment. The samples are post cured using convection oven to 150^{o}C for 30 minutes to see the variations in the prepared samples with post curing. Summer and winter conditioning is also done. This is achieved through an environmental weathering chamber, with temperature and humidity control.

Precautions:

1. Mixing Bowl is cleaned using laboratory cleaning solution to remove any dirt
2. Readings taken are accurate without any parallax errors.

4.2 Fourier Transform Infrared Spectroscopy:

Fourier transform Infrared spectroscopy provides information about the functional groups present inside the molecule. It is the measurement of Infrared (IR) frequencies absorbed by the organic sample placed in the path of the light beam [13]. Plotting absorbance or transmittance against the frequency yields infrared spectrum. An absorption band in the infrared spectrum gives information about the structure and bonding in the molecule

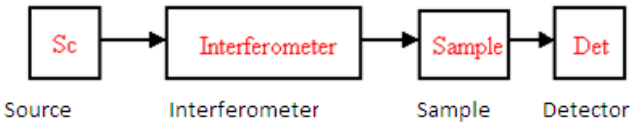

Figure 4-1: Flow chart of the FTIR process

Figure 4-2: FTIR table top apparatus [12]

The utilized FTIR system capabilities and specifications are as follows: Resolution up to 0.125 cm-1 is possible, Spectra can be collected at 20 scans per second, Spectral range :4000-400cm^{-1}, Detector: Deuterated triglycine sulfate (DGTS), Beam Splitter: KBr, IR Source : Ever Glovmid IR to Far IR Source, Tungsten Halogen

FTIR Experiments: Figure. 4-3 displays the FTIR plots of all the four samples discussed above (section 4.1). The FTIR apparatus used for this application is mounted with an endurance swap top operation, to help maintaining a uniform contact between the sample and the sampling surface.

Figure 4-5 shows enarged view of 911cm^{-1} peak Magnitude of 911 cm^{-1} indicates the amount of unreacted epoxy present in the mixture [14, 15]. As DGEBA reacts with the Hardener or initiator, its backbone is affected and epoxy ring opens to give hydroxyl groups which ultimately leads to increase in 3350-3500 cm-1 peak (Figure 4-4) due to increase in 2K reaction, which increases by increasing the mechanical quality between the resin and hardener groups.

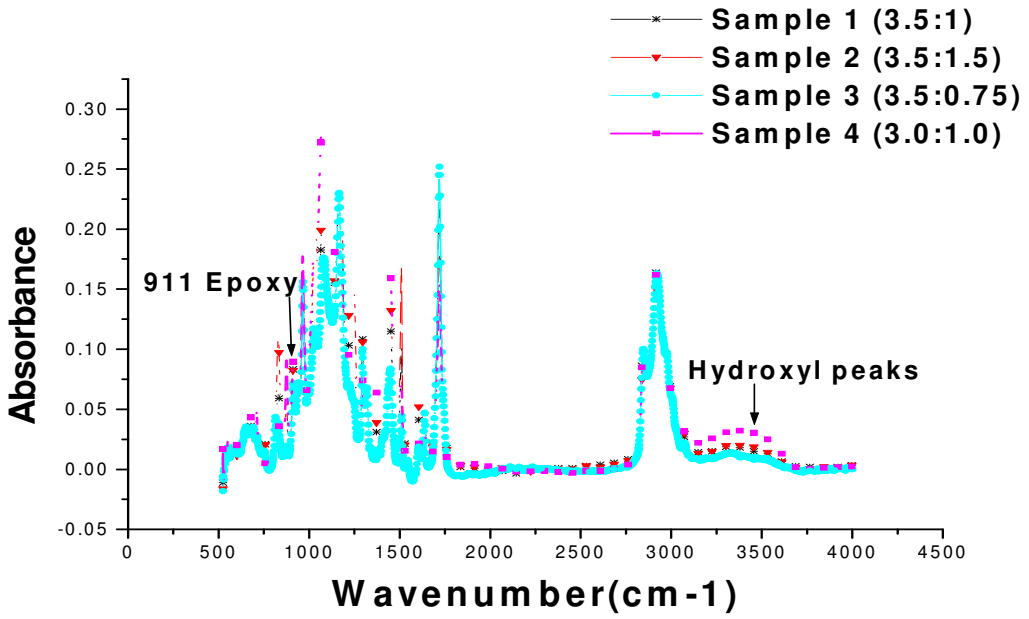

Figure 4-3: FTIR spectrum of four laboratory prepared samples

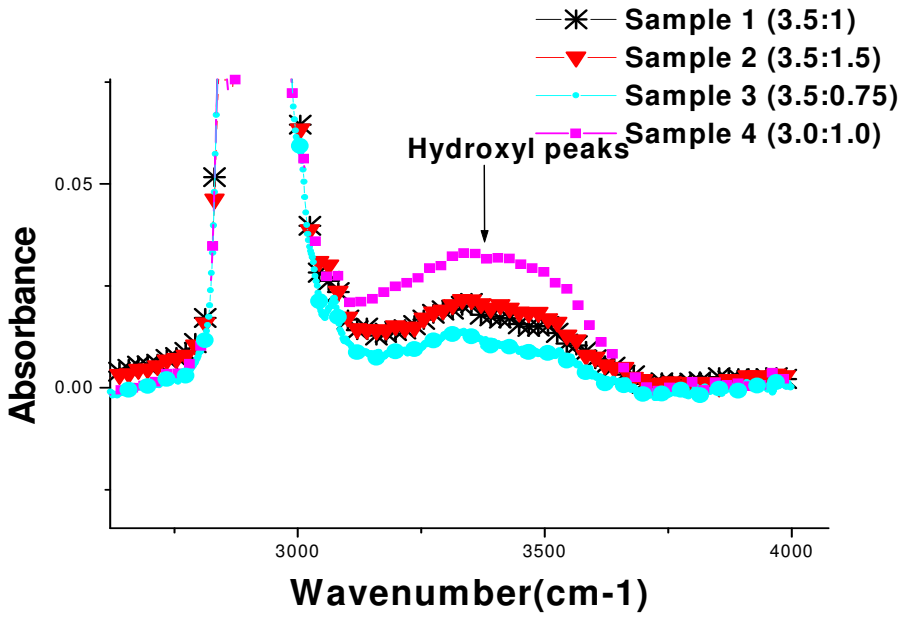

Figure 4-4: Variation in 3350 - 3500 cm-1 peak

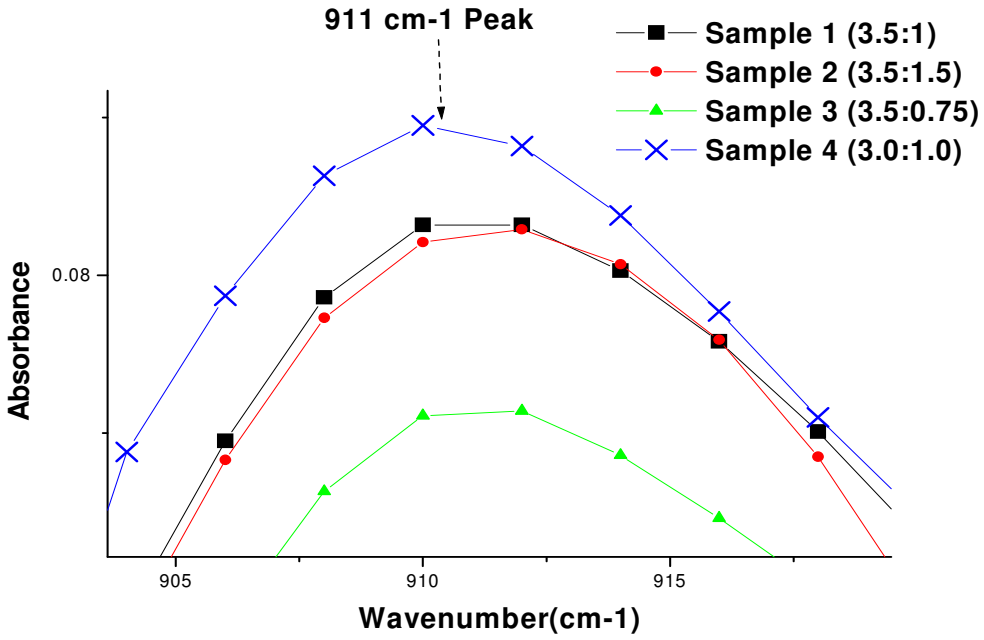

Figure 4-5: Variation in 911 cm^{-1} peak

According to Bockenheimer et al [16] peak growth in wavenumber range 1770 to 1620 cm^{-1} may be attributed to degradation of epoxy groups (figure 4-6). The breaking of many chemical bonds is considered to form new chemical groups such as C=O, C=N and alkenes. All these bonds have absorption band in the range of 1700 cm^{-1}. As per the following figure 4-6 the sample with higher hold time has higher magnitude peaks in this region and the sample with lower hold time has lower magnitude peaks which indicate an incomplete cure.

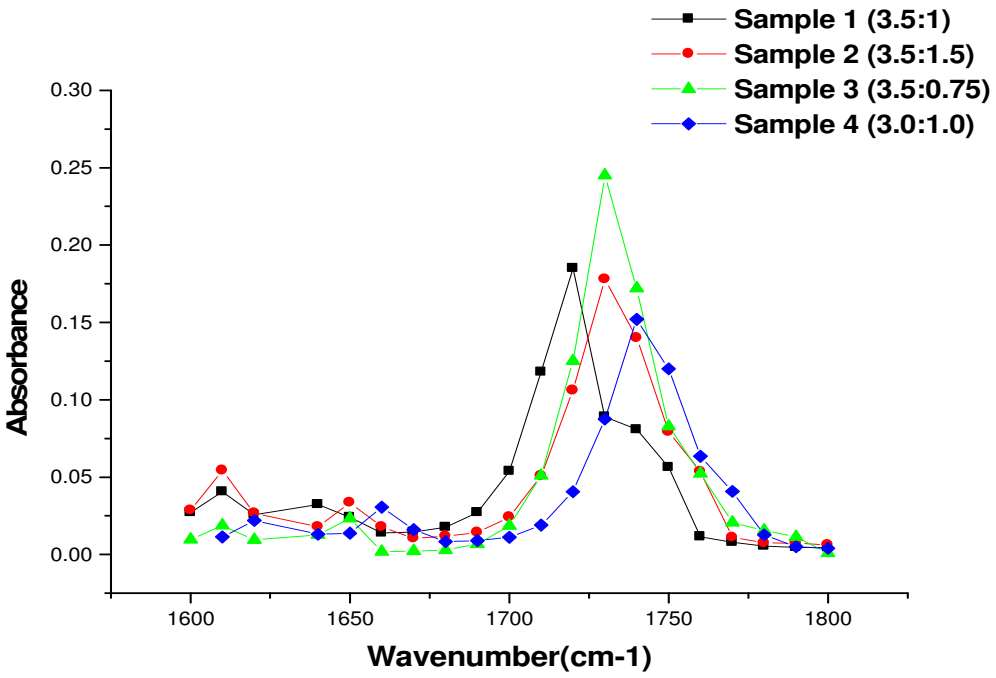

Figure 4-6: Peak growth between 1770-1620 cm-1

According to Bhatia et al [17], 1296 cm^{-1} peak is also a good indicator of the degradation and formation of the functional groups with the reaction. Figure 4-7 shows the variation in the 1296 cm^{-1} peak; the higher magnitude samples indicate that the sample is not yet completely cured where as lower magnitude peak indicates the completely cured sample. As per figure 4-7, the sample which is post cured using convection oven has lower magnitude peak than the sample which is not post cured.

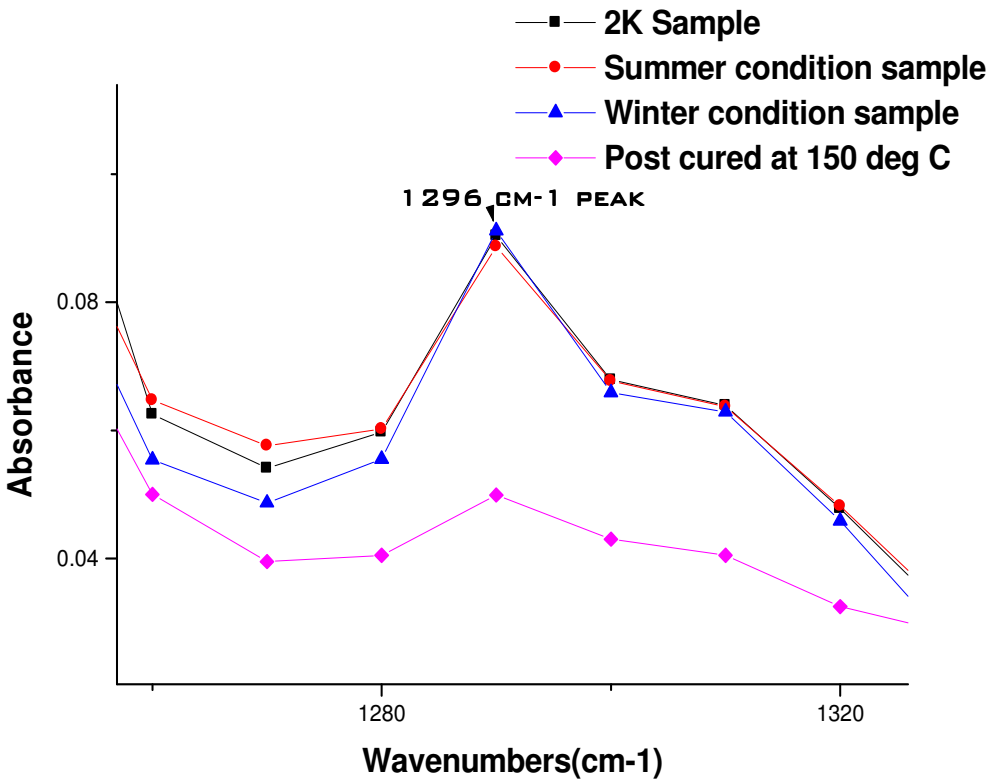

Figure 4-7: Variation in 1296 cm^{-1} peak

4.3 Differential Scanning Calorimeter

Basic Definition: This thermal analysis technique is used to measure the energy difference between a reference material and a test sample; at a particular set temperature and under identical temperature conditions, while being heated or cooled at a constant and controlled rate. DSC equipment is divided into two types based on the mode of energy input;

Power compensation DSC: Here the sample and the reference materials are controlled using different furnaces. Temperatures are adjusted to nullify the temperature difference

between the two furnaces and the energy spent to attain zero temperature is used to determine the enthalpy or heat capacity of the sample against the reference [24].

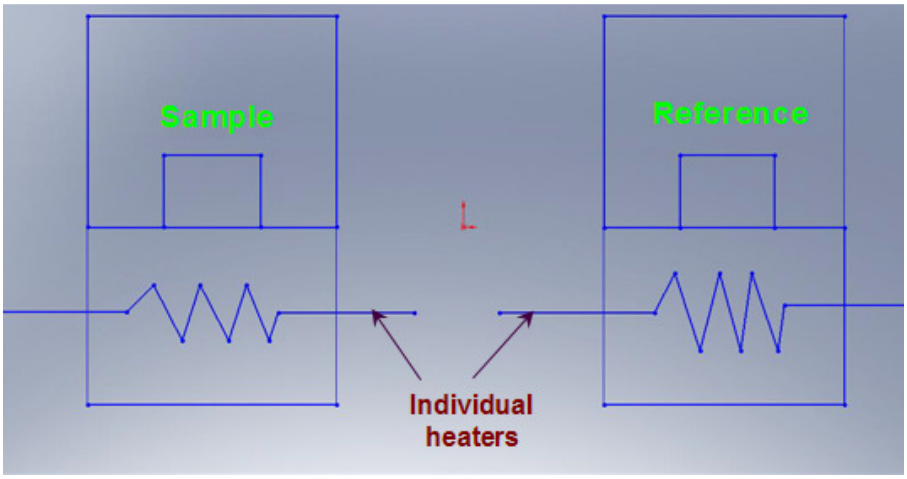

Figure 4-8: Power compensation Differential Scanning Calorimetry

***Heat flux DSC**:* Unlike power compensation DSC; the sample and the reference materials are heated in the same chamber. The reference and the sample are mounted on a metal disc. Temperature difference caused due to change in enthalpy or heat capacity is noted and related to enthalpy change by calibration experiments [24].

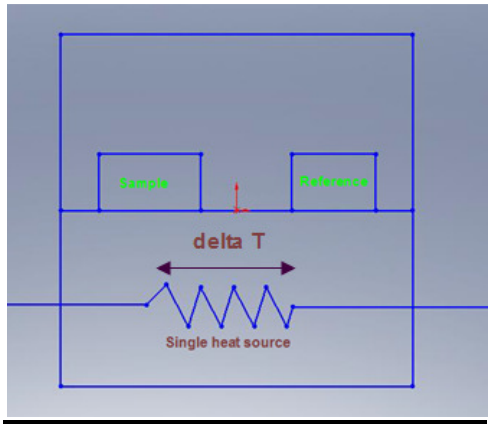

Figure 4-9: Heat flux DSC

DSC thermographs provide following information: Glass transition temperature (T_g), Melting temperature, Degree of cure with holding time, and the amount of anti oxidants in adhesive (if any). However, following precautions should be noted; the Samples which release large amounts of volatiles upon heating should not be loaded in the chamber. Also, the table on which the DSC is mounted should not be disturbed during loading of sample and experiment.

Sample preparation:

Samples that are to be loaded in DSC chamber are closed in the hermetic pans and weighed using a sensitive weighing balance. Hermetic pan and lid assembly resembles small flying saucer and can hold samples up to 20 milligrams, figure 4-10. Small hole is pierced on the lid to vent any volatiles that are generated during heating. These pans are generally made from aluminum and can withstand temperatures up to 600^{o}C.

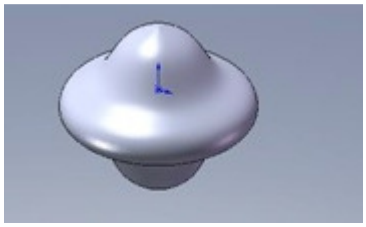

Figure 4-10: Hermetic pan and lid assembly

Experiment Objectives*:*

1. To determine the glass transition temperatures. This is to observe the point where a sudden change in viscosity of the two-component adhesive (2K) changes. Change in viscosity may lead to change in adhesive flow rate from the robot dispenser, which in turn leads to changes in fill rate, bead shape and volume.

2. To determine the effect of holding time on the curing-rate of 2K adhesive. The holding time is the time between application of adhesive bead and its final cure, in the E-coat oven. It may be due to the travelling distance between press shop and assembly shop, Die tooling changes and the production rate. Typically holding time of 1-3 days is considered for this case study.
3. To observe the affect of storage conditions on the glass transition temperatures.
4. The influence of amount of elastomers in the PVC based sealant, on glass transition temperature.

Apparatus:

Machine: TA Instruments Modular DSC 2920 Calorimetric device

Type of Purge: Nitrogen purge

Temperatures Range: 25 Deg C to 250 deg C

Ramp up rate : 10 deg C/min

Observations and discussions:

Determination of curing rate: To study this variation, two laboratory prepared samples with the nominal mixing ratio of 3:1 (Resin: Hardener) are considered. The DSC curves are generated to study the change in curing characteristics. DSC curve of the 2K sample held for 20 hrs in the laboratory atmosphere is shown in the figure 4-12 and the laboratory sample held for 48 hours is shown in the figure 4-11. From these figures, changes in the endotherms and the exotherms are clearly observed, indicating a change in the cure-rate. Furthermore, the sample with 20 hours holding is considered as a reference for the un-cured rate. The cure-rate difference between the two samples is quantified,

through computing the enthalpy of reaction for each sample. This is done by integrating the area under obtained DSC curves for both the samples. Equation 4.1 below gives the formula to compute degree of cure [1].

$$\alpha = \frac{\Delta H_{Un-cured} - \Delta H_{Cured}}{\Delta H_{Un-cured}} \quad (4.1)$$

Where $\Delta H_{\text{un-cured}}$ = Area under the uncured sample (Curve 1), ΔH_{cured} = Area under the cured sample (Curve 2), and α= Degree of cure (%)

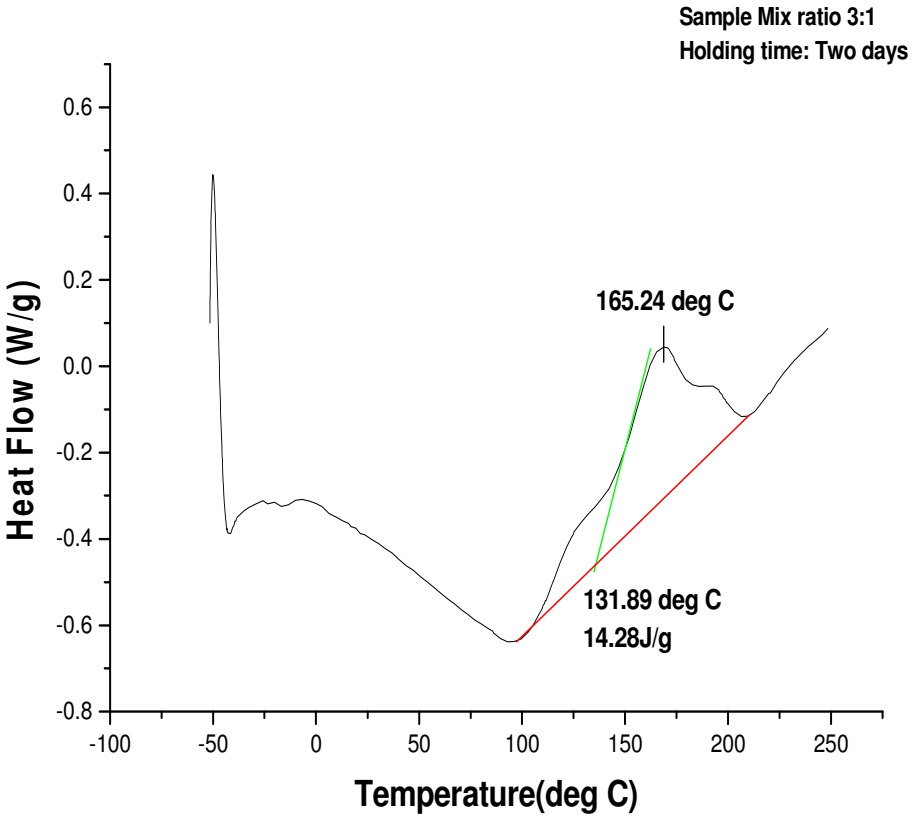

Figure 4-11: DSC curve of the 2K sample with 3:1 mixing ratio and hold time of two days

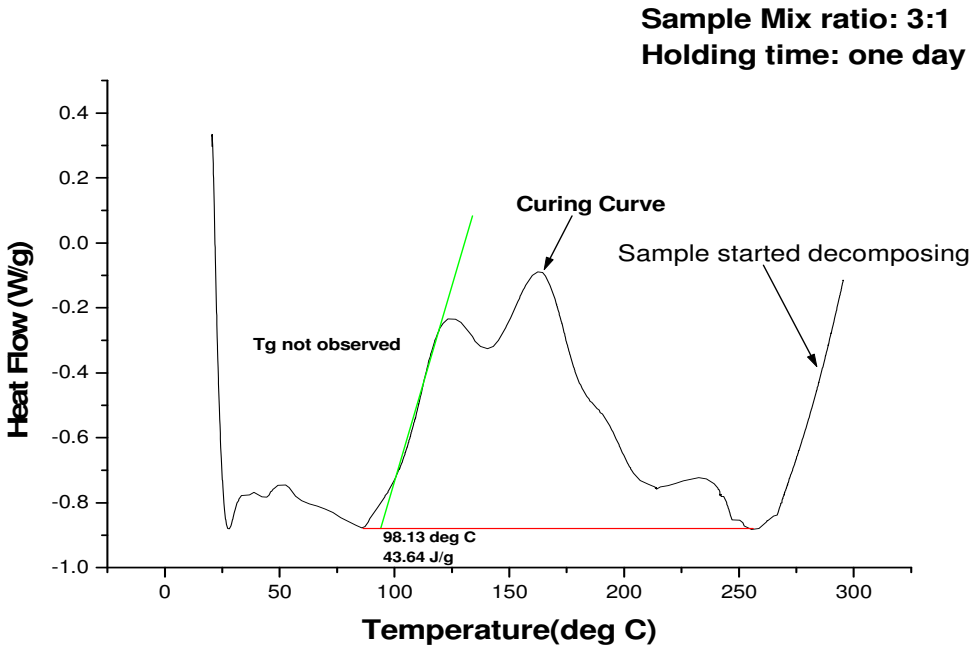

Figure 4-12: DSC curve of 2K sample with 3:1 mixing ratio and hold time of one day

Following observations can be made from above graphs (Figure 4-11 and Figure 4-12); Change in enthalpy of uncured sample ($\Delta H_{uncured}$) **= 43.64J/g,** Change in enthalpy of cured sample (ΔH_{cured}) **= 14.28J/g,** Substituting above values in equation 1 which yields $\alpha = (\Delta H_{uncured} - \Delta H_{cured}) / \Delta H_{uncured}$ = ((43.64-14.28)/43.64)*100= **67.27%.** An increase of 67.27% cure rate is observed is observed in the 48 hours sample than that of 20 hours sample due to increase in holding time of one day. The above method is repeated for all the production line and the laboratory samples with the mixing ratios (nominal ± 6%), resulting almost same cure rate value. The thermo-set cure rate influences the hemmed joint strength and the spring back effects that arise after hemming,

Effect of humidity on glass transition temperature:

Laboratory prepared and production line samples are subjected to different weather conditions that are based on data from the national weather center for local conditions; summer (Temperature= 38^{o}deg C, Relative Humidity= 85%) and winter (Temperature= 25^{o}C, Relative Humidity=50%). The samples are kept in environmental chamber and then transferred to DSC chamber for testing. One of the environmentally conditioned samples with the mixing ratio 3.2:1 tested in DSC chamber is shown in the following figure 4-13. Results show that there is sharp endotherm which may be due to the increase in volatiles release, because of weather conditioning.

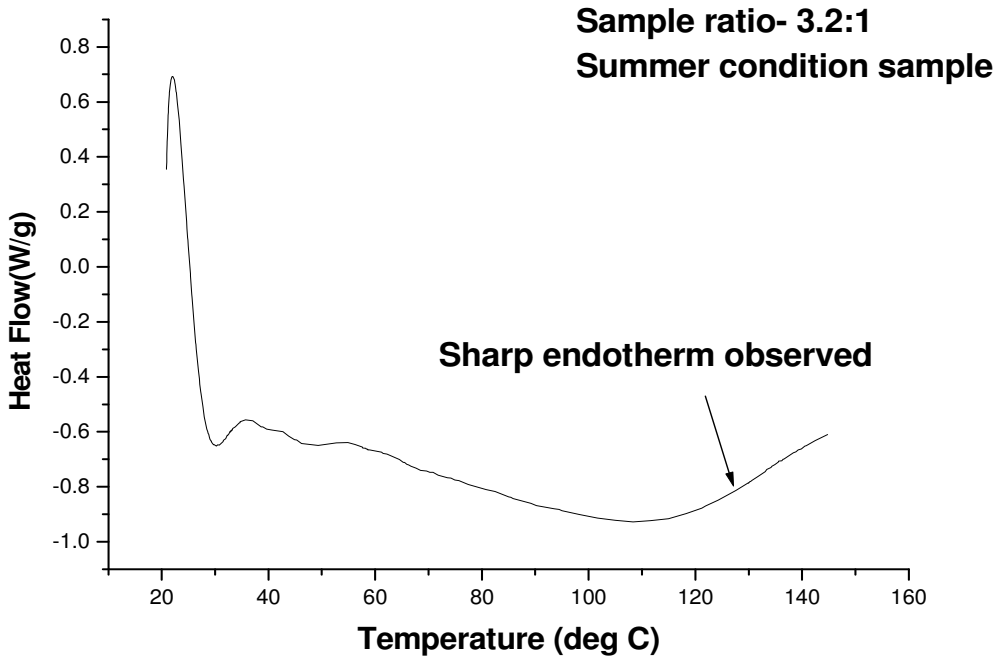

Figure 4-13: DSC curve of environmentally conditioned sample

Effect of mixing ratios on glass transition temperature

Upon observing four different automotive door assembly lines, a fluctuations of +/-6% in the two component adhesive mixing ratio is found, so four samples are prepared with following mixing ratios (Resin: Hardener on weight basis), 3.5:1.0, 3.5:1.5, 3.5:0.75, in addition to 3.0:1.0. All the four samples are loaded in the DSC chamber to observe the variations in the glass transition temperature (figure 4-14). Results indicate that there is only change of ±1^{o}C variation in glass transition temperature (T_g) with the change in mixing ratio.

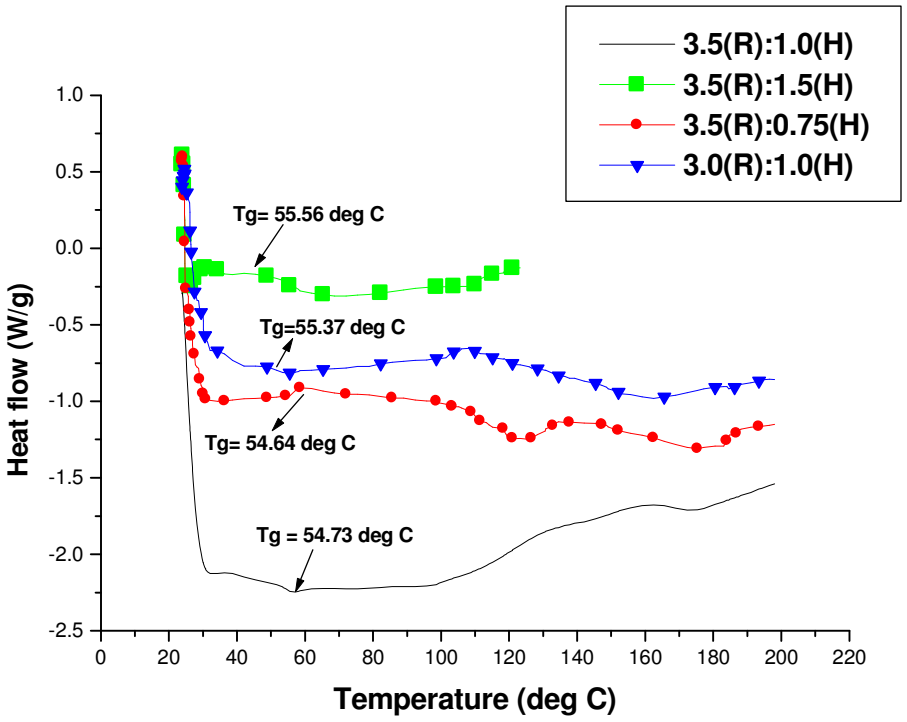

Figure 4-14: Glass transition temperatures of laboratory prepared samples

Influence of elastomers on the Tg of sealant:

PVC based sealant is collected from the production and loaded into the DSC chamber to observe the curing behavior and its glass transition temperature (figure 4-15). The sealant curing is not observed when subjected to high temperatures, because of the high percentage of plasticizers Di-Octyl phthalate present in it (from FTIR results). Also no sharp glass transition temperature (Tg) is observed, which might be due to the same reason.

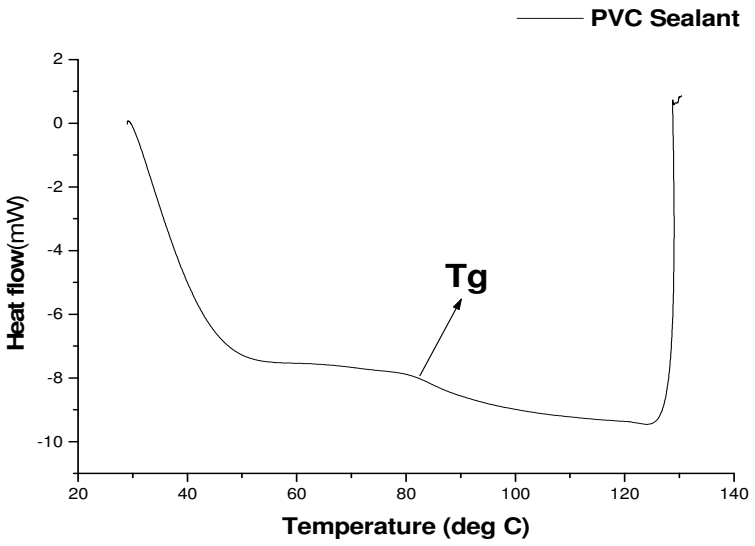

Figure 4-15: DSC plot of PVC based sealant

4.4 Thermogravimetric analysis

Thermogravimetric analysis is a thermal analysis technique by which changes in weight of specimen with time and temperature is measured and recorded. Unlike DSC, while performing TGA experiments, there is no need to weigh the specimen separately, TGA has its own inbuilt analytical balance with the crucible. This supports and guides

the specimen to the electrical furnace. In built plotter plots the weight change of the specimen with time and furnace temperature. Parameters that need to be considered while performing the experiment are the type of purge gas and its flow rate. The TGA is typically used to determine; Volatiles content, Moisture content, Effect of oven ramp up conditions, and the Effect of reactive atmospheres on materials. TGA does not require any special sample preparation

Experiment Objectives:

1. To determine effect of the environmental conditions (storage) on the volatiles release rates. Volatiles, moisture and atmospheric contamination may be absorbed by the adhesive in hem joint during storage or transportation. Volatiles can be a quality concern after application and curing of post hem sealant.
2. To determine the effect of oven ramp-up on the volatiles release. This is to identify the optimum oven conditions that may decrease the amount of volatiles release.

Apparatus:

Machine: TA instruments AutoTGA 2950HR V5.4A, Type of purge: Air purge (To simulate real time press shop conditions), Purge flow rate: 40 ml/min, Ramp up rate: Different ramp up rates.

***Observations and discussions*:**

Effect of environmental conditions on volatile release:

Summer condition:

Samples with mixing ratio of 3.2:1 are placed inside the environmental chamber, where summer conditions are imitated. The temperature and humidity values are taken from typical summer day in South Carolina; 38^{o}C and 85% RH. The samples are then transferred to the TGA chamber, to evaluate the volatiles release rate with different storage conditions. It is observed that the percentage of volatiles release in this case is almost equal to the volatiles release from the sample before storage. The plots of volatiles release is shown in figures 4-16 through 4-18. Plots show that the storage of the samples in these conditions has no influence on the volatiles release, detailed release rates are indicated in table 4-A.

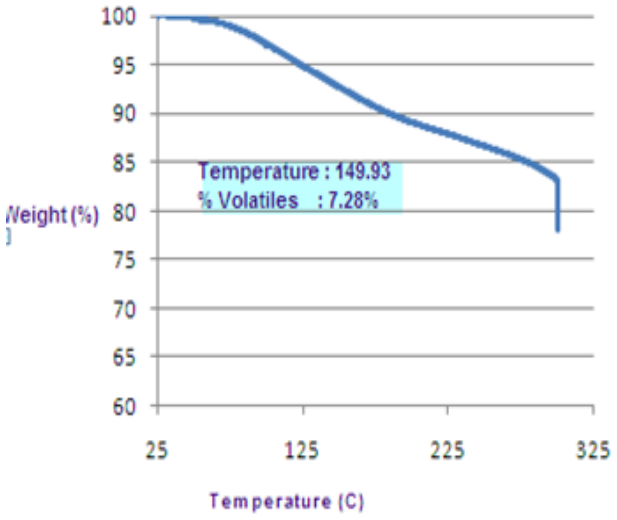

Figure 4-16: TGA analysis of sample with the mixing ratio of 3.2:1 and subjected to summer conditioning

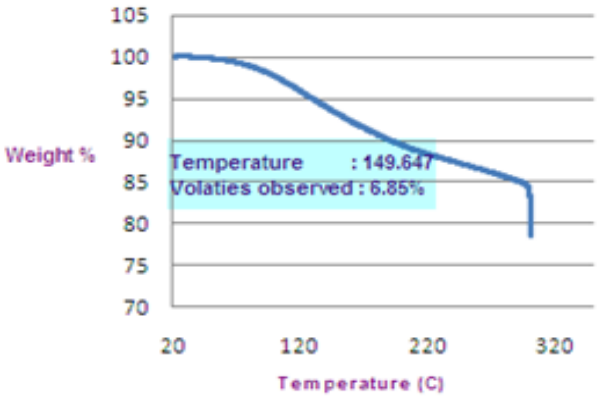

Figure 4-17: TGA of summer conditioned sample ramp up 20 C/min

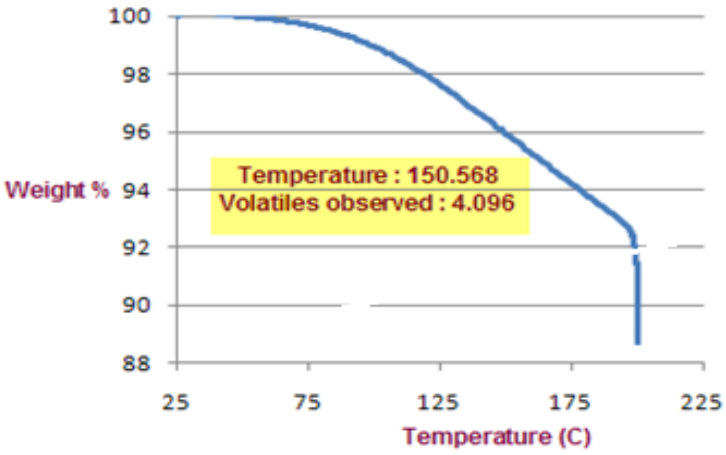

Figure 4-18: TGA of summer conditioned ramp up 30 C/min

Mixing ratio	Ramp up	% Volatiles
3.2:1	10	7.28
3.2:1	20	6.85
3.2:1	30	4.096

Table 4-A: Volatiles release from summer condition samples

Winter condition:

Samples with the same mixing ratio are placed inside the environmental chamber set to maintain winter conditions (25°C and 50% RH). A decrease in volatiles release is observed in this case when compared to the summer storage scenario. This might be due to the incomplete cure and the less absorption of moisture content from the atmosphere. The percentage of volatiles release and plots are shown in figure 4-19 through 4-21, with the results tabulated in table 4-B.

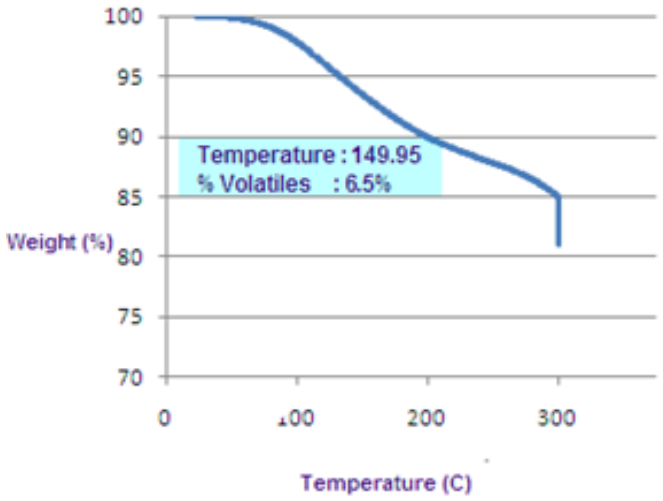

Figure 4-19: TGA analysis of winter conditioned samples subjected to ramp 10°C/min.

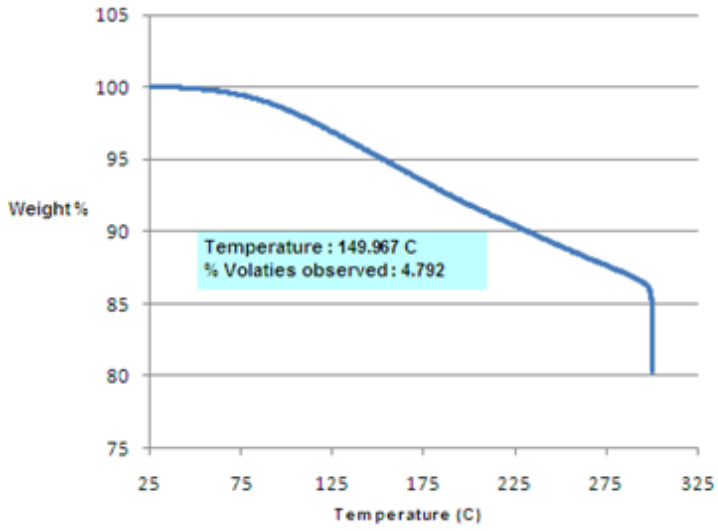

Figure 4-20: TGA analysis of winter conditioned sample subjected to temperature ramp 20^{o}C/min

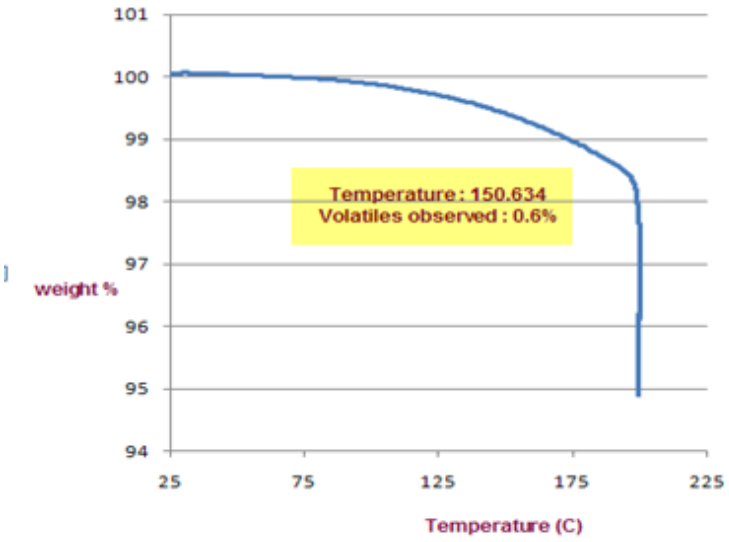

Figure 4-21: TGA analysis of winter conditioned sample subjected to temperature ramp 30^{o}C /min

Mixing ratio	Ramp up(C/min	Volatiles(%)
3.2:1	10	6.5
3.2:1	20	4.792
3.2:1	30	0.6

Table 4-B: Amount of volatile release from winter conditioned samples

Observations:

It has been observed that there is a slight increase in the percentage of volatiles released with the increase in the moisture content and the temperature when compared to room temperature samples. There is tremendous decrease in the volatiles rates with the decrease in the moisture content and temperature (winter condition sample). This indicates that the surrounding atmosphere's relative humidity affects the number of volatiles release during curing

Effect of oven ramp up on volatiles release:

Samples with mixing ratio of 3.2:1 are considered for experiments. Temperatures are raised up to 300^{o}C, different ramp up conditions such as 10^{o}C/min, 20^{o}C /min and 30^{o}C /min are used for the experiments. Figures 4-22, 4-23, and 4-24 are the corresponding plots obtained from TGA apparatus.

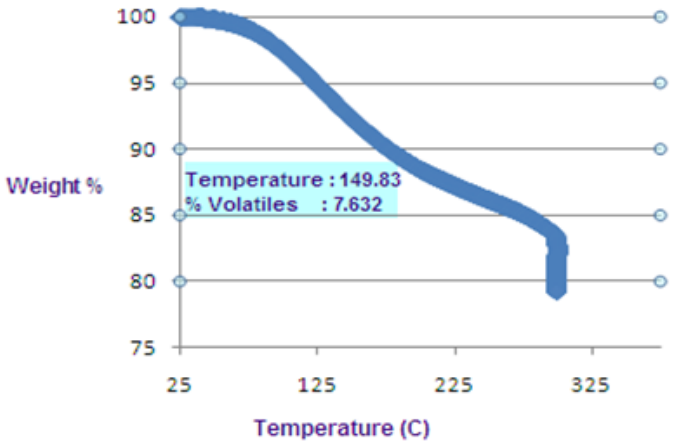

Figure 4-22: TGA analysis of 2K sample subjected to ramp up 10^{o}C /min

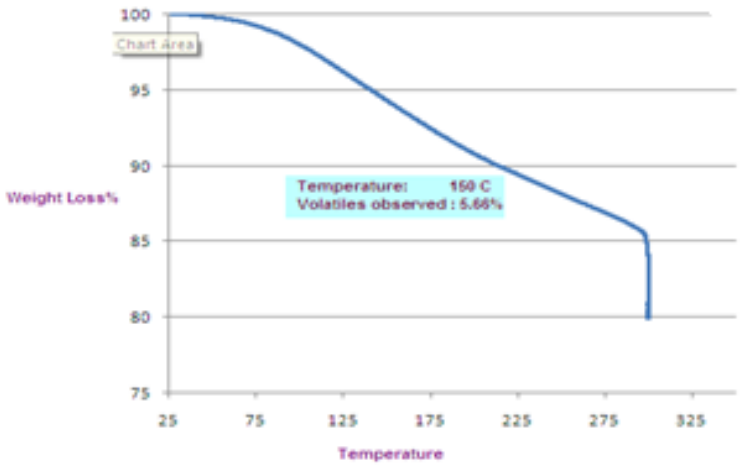

Figure 4-23: TGA of 2K sample with temperature ramp up of 20°C/min

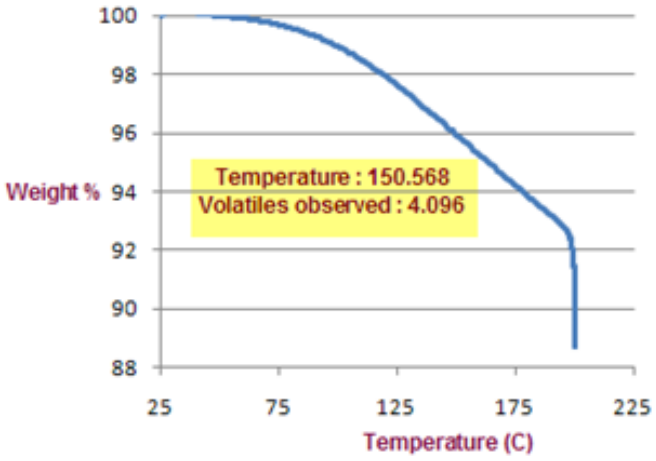

Figure 4-24: TGA of 2K sample with temperature ramp up of 30°C/min

Mixing ratio	Ramp up	% Volatiles
3.2:1	10	7.632
3.2:1	20	5.66
3.2:1	30	4.05

Table 4-C: Volatiles release rate of 2K sample with the variation of ramp up rates

Inference from the above graphs is that when ramp up rate increases, the volatile release depends upon the time that sample spends in the combustion chamber (Table 4-C). Volatiles may be due to the evaporation of gases entrapped during mixing of resin and hardener, chemical decomposition of the molecules [19]**.**

4.5 E-coat oven curves

These TGA experiments are designed to simulate oven curves of E- coat and UBS ovens. In figure 4-25 three stages; oven ramp up, hold and cool down are shown.

Experiment Objectives:

1. To determine the total volatile release from the 2K adhesive sample for each ramp up cycle 10^{o}C/min, 20^{o}C/min and 30^{o}C/min in E-coat oven
2. To determine percentage volatile release when PVC based sealant is applied over 2K adhesive. Here UBS oven conditions are simulated and volatile release is computed for different ramp up conditions

Experimental conditions:

Conditions for the first stage of experiment; Type of purge: Oxygen purge, Oven: E-coat oven, Peak Temperature: 160^{o}C, Holding time: 30 Minutes

Conditions for second stage of experiment; Type of purge: Oxygen purge, Oven: sealant oven, Peak temperature: 120^{o}C, Holding time: 15 minutes.

Results and discussions:

First stage results:

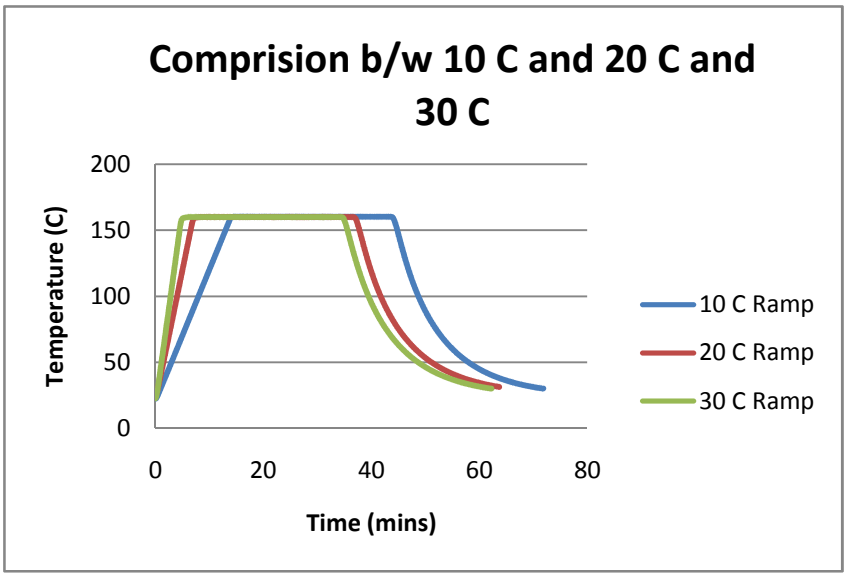

Figure 4-25: E Coat oven conditions with different ramp up conditions (only adhesive)

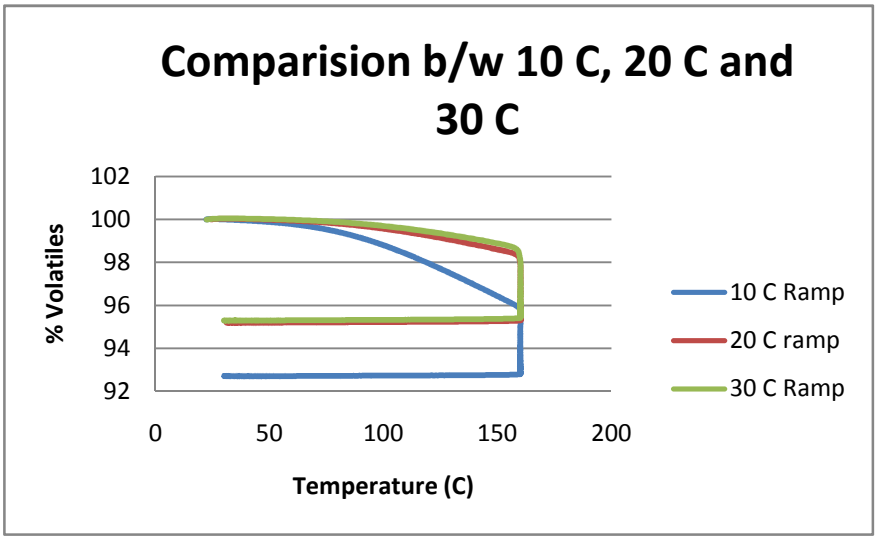

Figure 4-26: E coat oven conditions (% volatiles versus temperature)

Inspecting figures 4-25 and 4-26; Volatiles release during 10°C /min = 7.22%, Volatiles release during 20°C /min = 4.59%, and Volatiles release during 30°C/min = 3.24%. This leads to following conclusion;

As seen from the above trend as ramp up rate increases, volatiles release decreases. This may be due to the fact at higher ramp up the adhesive cures faster there by suppressing the volatiles release. [18]

Second stage results: It has been observed that; Percentage of volatiles release is almost all the cases, Percentage of volatiles release is low at 30 C/min

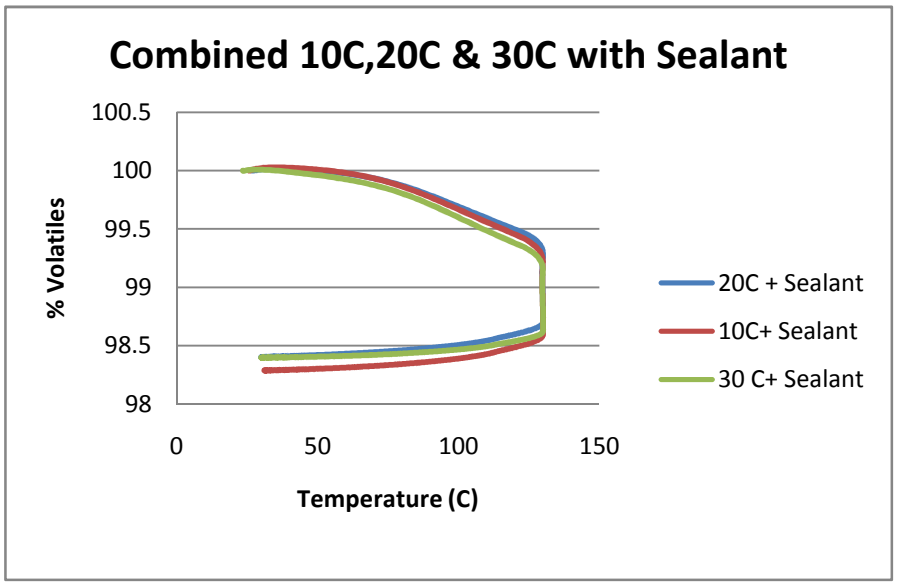

Figure 4-27: UBS oven conditions (Adhesive+ sealant)

4.6 Estimation of flange fill by using micrographs

According to Adams [4] to achieve corrosion resistant and void free joint it is necessary that the joint is completely filled by the adhesive as shown in the figure 4-29 below. Incomplete filled joints can act a buffer for the atmospheric air which expands

when joint is cured in the curing oven. If expanded air does not find enough space to escape it may lead to leakage and bubbles in the cosmetic sealer.

Following experiment is designed to monitor variation in the flange fill rates.

Apparatus Used:

Hand held microscope, Vernier calipers, Desktop computer with the Matlab code running on it.

Experimental procedure:

Surface to be photographed must be held between the magnets without disturbing the former. Capture the required image, measure pixel values of all the ten dimensions, Note down all the dimensions, and Compare the observed dimension with the standards to study capability.

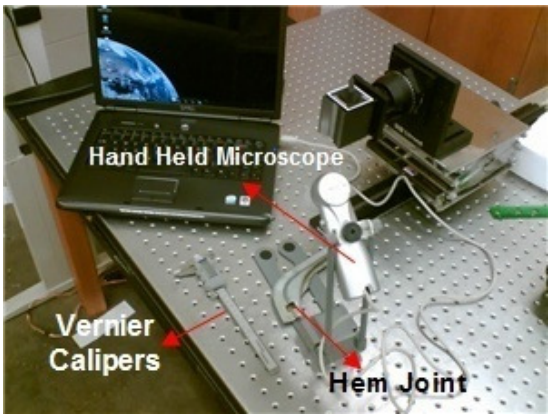

Figure 4-28: Apparatus Used to measure flange fill

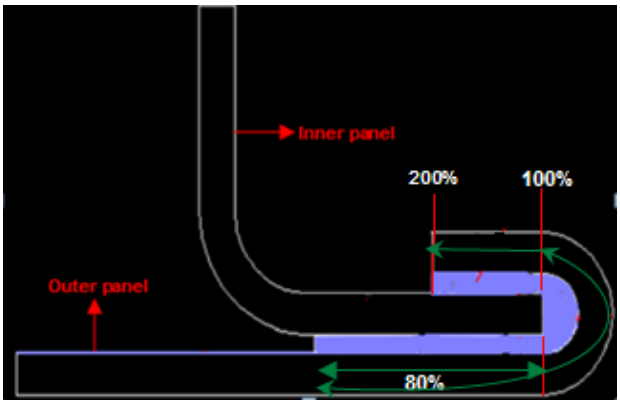

Figure 4-29: Hem flange showing various fill levels

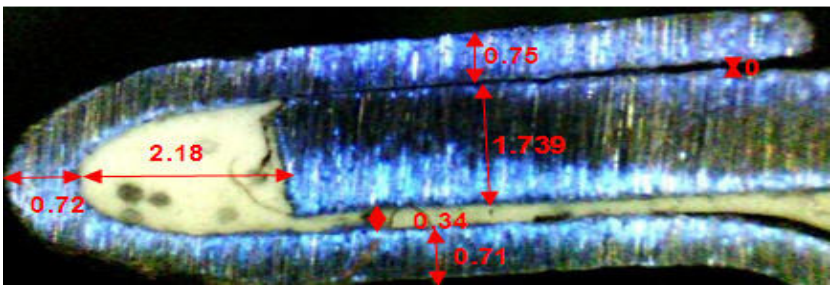

Figure 4-30: Sample micrograph of hem joint with fill rate of 100%

4.7 Determination of gel point of PVC based sealant

To determine the gel point of PVC based sealant, which helps in predicting the curing time and temperature inside the sealant oven. The gel point is where the viscosity of the adhesive or sealant raises due to the increase in its average molecular weight. At this point the sealant behaves as pseudo elastic, by virtue of which the sealant can no longer be applied. While, the gel time is between the point of application of the sealant and the gel state, where movement between the molecules ceases.

Experiments designed to determine the gel point:

Apparatus needed*:* FLIR uncooled micro-bolometric camera with tripod stand, Hot plate, Acquisition software and PC.

Figure 4-31: Apparatus used to find gel point of PVC sealant

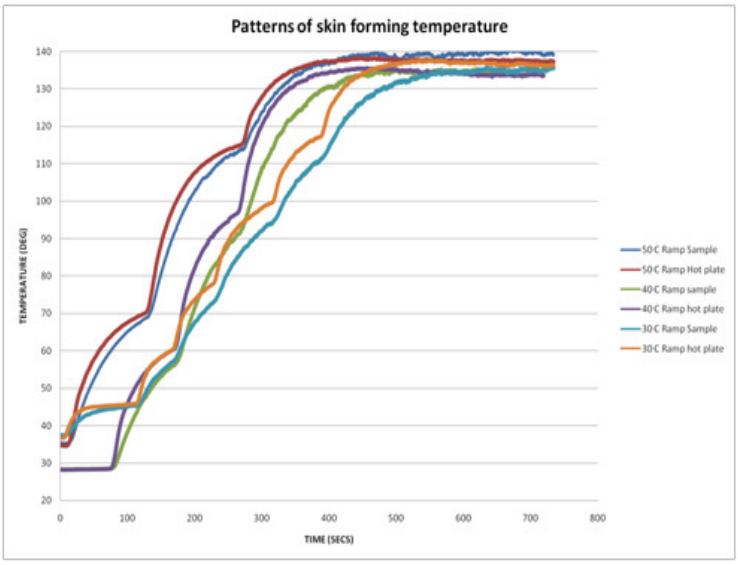

Figure 4-32: Plot from FLIR un-cooled camera

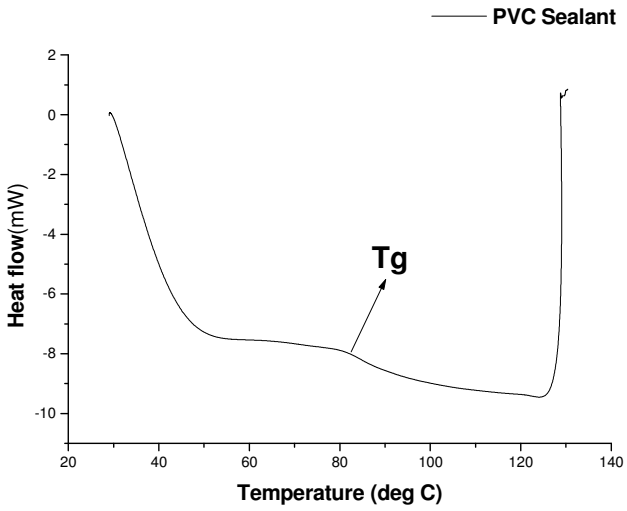

Figure 4-33: DSC cure of PVC based sealant

Above figure 4-32 shows the graph that is obtained from the thermal camera. Basically a sealant layer (0.8 mm) is applied on the hot plate, which is calibrated according to the sealant oven temperature profile. The time and the corresponding

temperature are noted, when the first change of sealant is observed. The experiment is repeated for different ramp up rates and the readings are tabulated, in table 4-D.

Ramp up	Skin forming temp	Skin forming time
30 C/min	55	1.83 min
40 C/min	70	3.16 min
50 C/min	80	2.33 min

Table 4-D : Skin forming temperatures at various ramp up rates (Hot plate)

Results:

Curves collected from hot plate experiment and from DSC chamber (Figure 4-33) are compared with each other. Results show that the values are correlating.

CHAPTER 5

5 Conclusions and future work

This manuscript introduced the usage of the DSC, FTIR, and TGA analyses, to investigate the process variations impact on non-load bearing adhesives, used for automotive hem-flanges. The FTIR investigation provided information about the different peaks indications; the 911 cm^{-1} is used to investigate the mixing ratio of the resin and hardener; showing a resolution of ±6% in current epoxy ratio, while the 3350 – 3500 cm^{-1} peak is used to study the early cure using the hydroxyl group, and hence the mixing quality. Changes of peak magnitudes in the region 1770 cm-1 to 1620 cm^{-1} is also observed. It has been observed that 1296 cm^{-1} peak can be a good indicator of the degradation of the various functional groups due to the reaction. Further, the DSC is used to quantitatively decide on the cure rates for samples held at different holding times, where a 67% cure-rate difference is computed between samples held for 1 and 2 days, which is found to be independent of the mixing ratio. Lastly, the TGA curing provided information about the adhesive sensitivity to the weather conditions and the relative humidity levels. It has been observed that storage conditions do have impact on the volatile content of the current automotive two-component adhesive. Less volatiles are observed in the winter conditioned samples. Influence of flange fill rates is high on the moisture entrapment and volatile evaporation rate. Additionally, new findings are reported about the effect of the curing profiles on the adhesives' volatile evaporation rates, mainly the ramp-up region. Briefly, this manuscript introduced and discussed the

evaluation procedures and criteria that might be used, when discussing the impact of the hemming process variations on a non-load bearing adhesive, especially those used for automotive hemmed joints.

Future work include; the identification of the expansion or the contraction in the 2K adhesive using ThermoMechanical analyzer (TMA), and the identification and analysis of the viscoelastic behavior of two-component adhesive using Dynamic mechanical analyzer (DMA). Also, the Thermal imaging techniques may be applied to detect the adhesion problems due to the creation of the voids, bubbles inside the adhesive which are responsible for the lack of adhesion. Furthermore, a full quantitative analysis of FTIR graphs to determine the mixing ratios using FTIR peaks.

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